1 Occurrence and Pathways of Organometallic Compounds in the Environment—General Considerations

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1.1 SCOPE OF THIS WORK

The compounds considered in this work are those having metal–carbon (normally metal–alkyl) bonds, and which have environmental implications or properties. There is limited reference to metal–carbon \( \pi \) systems (e.g. \( \text{Mo(CO)}_6 \), \( \text{W(CO)}_6(\text{\( \eta \)-CH}_3\text{C}_5\text{H}_4\text{Mn(CO)}_3) \)) and mechanistic discussion of metal hydrides and ethene (e.g. decomposition by \( \beta \) elimination). In terms of formation of organometallics, methyl groups predominate but there is also reference to other metal hydrocarbon compounds (e.g. ethyl or phenyl mercury, ethyl leads, butyl tins). However, much of this work refers to metal methyl compounds as these are formed naturally in the environment (biomethylation).

The thrust of the work involves a good deal of analytical chemistry, but that is not the prime focus of the book. However, without the modern developments in analytical chemistry of the past 50 years, knowledge of most of the chemistry described in this book would barely exist. The analytical work that has led to this chemistry is described in the appropriate chapter but it is not the main theme. Several recent and comprehensive works that focus on the analytical chemistry of the environment have recently appeared and the reader is referred to those for the technical details of the analytical chemistry (see Standard Reference Sources and References at the end of the book).
Amongst these, the recent comprehensive work by Crompton [1] focuses almost exclusively on the analysis of metal cations with minor consideration of organometallic compounds, and as its title denotes, is concerned with analysis from aqueous media. Similarly the work of Ure and Davidson [2] is mainly directed towards metal cations. The recent work edited by Ebdon et al. [3] also focuses more on analytical chemistry but takes full account of the complete molecular identity of the metallic compounds present (not focusing exclusively on organometallic compounds), i.e., speciation. (The importance of speciation is discussed later.)

Given that the stability, transport and toxicities of organometallic compounds depends on the number and type of the metal alkyl or aryl groups present, and that different compounds of the same or different metals may coexist at the same location in the environment, then separate detection of each species (speciation) is necessary. Separation and detection go together in so-called interfaced or hyphenated analytical systems. This is of particular importance because such species, although having real environmental and/or toxicity effects, often occur at very low concentrations in the environment (ppb, ppm—see later for definitions).

Nevertheless a broad statement on analysis needs to be made. There are two considerations:

(i) The metal, organometallic fragment or full compound needs to be detected by a sufficiently sensitive method (e.g. Hg, CH$_3$Hg$^+$, CH$_3$HgCl respectively), and
(ii) as a variety of organometallic compounds of the same element may be present together in the same matrix (e.g. butyltins, butyl/methyltins) and they each have different toxicity and environmental properties, then they must be separated before individual detection.

The main methods of detection are as follows:

(i) Atomic absorption spectroscopy (flame, graphite furnace, Zeeman, hydride generation/quartz furnace),
(ii) atomic fluorescence spectroscopy (alone or via hydride generation),
(iii) atomic emission spectroscopy (usually inductively coupled plasma),
(iv) voltammetry,
(v) mass spectrometry (conventional or chemical ionization, electrospray, tandem, isotope dilution, plasma),
(vi) X-ray and neutron methods.

The main methods of separation are:

(i) Gas chromatography (conventional or capillary),
(ii) thermal desorption methods (which depend on boiling points),
(iii) high performance liquid chromatography,
(iv) flow injection methods,
(v) ion exchange chromatography,
(vi) ion chromatography.

Many organometallic compounds, or cations are insufficiently volatile to undergo gas chromatography, but may be induced to do so by derivatization. This is generally achieved by (formally) SN₂ attack by hydride (from NaBH₄), ethyl (NaB(C₂H₅)₄) or other alkyl group (e.g. from a Grignard reagent), e.g. Equation (1.1)

\[ \text{As(CH₃)₂X} \xrightarrow{\text{NaBH₄}} \text{As(CH₃)₂H} \]  

(1.1)

X = environmental counter ion (in this case not riboside—see Chapter 5)

This has been widely achieved, even in the case of mercury where it had been thought that mercury hydrides were too unstable for use in analysis [4].

Coupling of these separation and detection techniques is now ubiquitous and provides an intensive battery of techniques for analytical work, well described in Reference [3]. Without these, little knowledge of organometallic compounds in the environment would be possible.

The present work is also not primarily a work of toxicology although the toxicity properties of the compounds are discussed in the chapters element by element. The reader is referred to several excellent works specifically dedicated to toxicity studies of organometallic compounds [5].

The present work is a consideration of the inputs (natural and anthropogenic) and/or formation of organometallic compounds in the natural environment (sediment, water and atmosphere), their properties and behaviour there, and their ultimate fate. Although much of our understanding in this field is derived from analytical chemistry and the methods are described where needed, the theme of the work is the overall behaviour of organometals in the environment, not their analysis. Compounds are covered by chapters on an element-by-element basis.

Organometallic species (i.e. compounds, complexes or ions) may be found in the natural environment either because they are formed there or because they are introduced there. To date, the behaviour of the latter group is better understood, and their environmental impact has been assessed by studies of their direct toxicities, their stabilities and routes to decay, and by toxicity studies of their decay products. Organometallic compounds entering the environment may be deliberately introduced as products whose properties relate to the environment (e.g. biocides) or they may enter peripherally to a separate, main function (e.g. gasoline additives, polymer stabilizers). Compounds of arsenic, mercury, tin and lead have important uses as organometallic compounds. Their role and behaviour in the environment are covered in the appropriate chapters of this work (Chapters 2 to 5). The behaviour of other organometallic species in the natural environment is also covered (Chapters 6 to 10). However, not all organometals found in the environment are introduced—some are formed
after entry as inorganic species and constitute the organometallic components of global biogeochemical cycles. This process of environmental methylation is usually termed biomethylation and is, as the name implies, almost exclusively concerned with formation of metal–methyl bonds (although ethyl mercury has been found in the environment in circumstances removed from likely input as a product). Recent work has demonstrated the occurrence of transition metal carbonyls, likely to have been formed in the environment (see below).

1.2 GENERAL APPROACH: SPECIATION, CONCENTRATIONS AND TERMINOLOGY

This work considers those organometallic compounds that have relevance to the natural environment. It is concerned with compounds that are found there, or which may be formed there, or which may react or be transported within the environment. Accordingly we discuss inputs, formation, transportation and decay. The approach is to consider these processes element by element in each chapter. The present chapter links the work by considering those fundamental aspects of organometallic chemistry that are relevant to the environmental chemistry of the elements discussed in each chapter, including stabilities, and mechanisms of environmental formation and decay.

It is at this point that further consideration of the term ‘speciation’ should be made. A generation ago, and indeed much legislation concerning pollution, etc. still occurs in this context, chemists had to be content with discussing a contaminant by its defining element (e.g. total arsenic, mercury concentrations, etc.). In parallel with many chemists becoming environmental chemists, technology and necessity prompted further identification into partial or complete molecular identification of the contaminant (e.g. methylmercury, CH$_3$Hg$^+$, arsenobetaine, (CH$_3$)$_3$AsCH$_2$COO$^-$). Such full operational identification of a compound within a larger matrix is now commonly termed ‘speciation’. Where possible, to accord with a speciation approach, we will discuss the chemistry in terms of compounds.

Additionally of course, speciation is now not only more possible, it is essential. The main toxicity and environmental properties depend markedly on what compound is present, not on what metal. Some arsenic compounds are notoriously toxic (e.g. As$_2$O$_3$), but some are effectively non-toxic (e.g. arsenobetaine). Toxicity also depends on the degree of alkyl substitution of a metal and the identity of the organic (alkyl) group, and it varies also for the same compound towards different (biological) species. Residence times may also vary with species (e.g. CH$_3$Hg$^+$ (long) and Hg$^{2+}$ (shorter) in biological tissue), and this can determine toxic impact. In addition to toxicity, transportation parameters also vary for the same element with its speciation, e.g. partition to atmosphere or water. Organometallic cations (e.g. Bu$_3$Sn$^+$) tend to be more water soluble and non-volatile, but saturated compounds (e.g. (CH$_3$)$_4$Pb) are hydrophobic and volatile.
Additionally, a generation ago analytical chemists had generally to accept quantitative limits for their work of parts per thousand (ppt or mg g\(^{-1}\)) e.g. for arsenic in a matrix (containing medium). At the time of the first edition of the present work (1986) parts per million or billion (ppm, ppb or \(\mu g\ g^{-1}\), ng g\(^{-1}\)) were being achieved. The standard now is commonly ppb (or ng g\(^{-1}\); the quantity present in 10\(^9\) parts of the matrix), but parts per 10\(^{-12}\) (ppt or pico grams per gram (fg g\(^{-1}\)) are now commonly reported. It should always be borne in mind how relevant in practical terms such extreme measures of dilution might be, and analytical and environmental chemists should pause on occasion to consider which chemical species may not be present in a matrix at fg g\(^{-1}\) or more dilute levels. Chemical analysis is usually targeted towards the species of interest and much else present may be missed or ignored. The question is, 'if the level of a certain species is of the order of 10\(^{-12}\) parts per gram, does it matter and if so, to whom?'

The above considerations also bring forward another point of terminology. Laboratory chemists usually express concentrations in molar terms, i.e. mol dm\(^{-3}\). At greater levels of dilution parts per million (ppm) and similar terms are often used. These terms are less precise, often because the matrix in which the species of interest is present is not water or a similar solvent. It is often a wet, amorphous sediment. Hence ‘ppm’ can mean one of the following:

(i) grams of the relevant atom present in 10\(^6\) grams of the matrix,
(ii) grams of a defined part of the molecule in 10\(^6\) grams of the matrix,
(iii) grams of the whole molecule in 10\(^6\) grams of the matrix.

In some published work, ‘ppm’ is not even defined as above. To add to the imprecision, the matrix (which may be a sediment or biological tissue) may be taken as wet (heavier) or dried (lighter)—giving two possible figures for the same measurement. Clarity of definition is not always present in quantitative work in this field, and the matrix is rarely the simple defined volume of known solvent that occurs in laboratory chemistry.

With regard to atmospheric or liquid measurements, terms such as ppm could mean:

(i) grams of the molecule (or relevant atom) present in 10\(^6\) cm\(^3\) of atmosphere (at STP?) or water, or
(ii) volume (cm\(^3\)) of the molecule (or relevant atom) present in 10\(^6\) cm\(^3\) of atmosphere or water.

Care therefore needs to be taken when results from different laboratories or groups are compared. Consistency is often absent (even orthodox molar concentrations are sometimes used, even at extremes of dilution).

To put this field into perspective—although ppm, ppb and similar concentrations can be of major physiological, toxicological or environmental
significance, it will do little harm to repeat the comparison given in the first edition of this work—a ppm is equivalent to a needle in a haystack; a ppb is equivalent to a grain of sand in an Olympic-sized swimming pool (in checking the calculation the reader is also invited to consider this as a not completely outlandish example of the use of imprecise concepts to register concentrations).

Within the present work, full standardization of terms is not possible owing to wide differences in practice, methods, matrices and analytical feasibility. To overcome this as far as possible, a basic attempt at standardization has been made and cross-referencing will then be used to clarify detailed points.

1.3 TYPES OF ORGANOMETALLIC COMPOUND

Most, but not all, organometallic compounds of environmental interest are covalent, bound by a σ bond from a single carbon atom, to a main group element. The term ‘organometallic’ is generally defined as a compound with a bond (M—C) polarized $M^{\delta^+}—C^{\delta^-}$ i.e. the metal is less electronegative than carbon. A compound containing carbon atoms, but where the bonds to the metal are not directly to the carbon atom (but may be via oxygen, nitrogen or halogen atoms instead), is not considered to be organometallic, although such a compound may be referred to as ‘metal organic’. In general then, the compounds discussed in this book will involve carbon bound to a main group metal via a single carbon atom—these are referred to as ‘monohapto’ compounds. Despite the polarization above, in this work metal–carbon bonds are usually shown as $R_nM$ to accord with common practice.

A vast organometallic chemistry of interest to synthetic and mechanistic organometallic chemists exists outside the definition above, which is of little significance (so far as is known) in an environmental context, other than by way of input from manufacture or use, in which case the pollutant is a decomposition product that is usually non-organometallic. (Transition metal organometallics have hugely important uses as synthetic and catalytic intermediates, but there is usually little pollution owing to the high cost of the metals concerned, e.g. rhodium, ruthenium, etc.) Within the context of these transition-metal compounds there are actually some instances of environmental significance, for example, ($\lambda$-CH$_3$C$_2$H$_4$Mn(CO)$_3$) is used as an anti-knock agent in gasoline (Chapter 9) and Mo(CO)$_6$ and W(CO)$_6$ have been detected in the environment (Chapter 9).

Most of the ‘metals’ in the present work are clear cut main group elements (mercury, tin, lead, etc.) but certain ‘metalloidal’ elements are included because their environmental properties have so much in common (arsenic, antimony, etc.). Some elements generally considered to be non-metallic have strong interactions with this area of work and are mentioned as needed (e.g. sulphur, selenium). Polymeric organometallic compounds are covered in the chapters relating to siloxanes (Chapter 8) and tin (Chapter 3).
1.4 THERMODYNAMIC STABILITIES OF ORGANOMETALLIC COMPOUNDS

As noted above, most of the organometallic compounds in the present work involve covalent bonds between a carbon atom (usually in a methyl, \( \text{CH}_3 \), group) and a main group (non-transition element). Such bonds may have little or much polarization (polarization is a measure of the drift in electronic charge in a covalent bond from, in this case, the metallic element to the carbon atom, viz. \( \text{M}^{8+} - \text{C}^{6-} \)). Polarizations vary and affect stabilities considerably. In general the \( \text{M} - \text{C} \) bonds can be considered as localized (albeit polarized) with conventional \( \sigma \) electron pair bonds similar to those occurring in organic chemistry.

In considering stability, we have to ask stability with respect to what phenomenon (hydrolysis, oxidation, thermal). We consider stability of a compound with respect to decomposition into its own elements (this doesn’t usually happen) and towards external chemical attack (the norm), e.g. by atmospheric oxygen, water and microbial-mediated decay. We consider inherent (thermodynamic) stability first because the general approach is helpful. However, in general it can be said that where the compounds are unstable it is not because of weak \( \text{M} - \text{C} \) bonds (thermodynamic) but because there are low energy pathways to decomposition (kinetic). A component is thermodynamically unstable with respect to decay to elements if the standard Gibbs free energy for the process is negative. In certain equilibrium reactions where this equals zero, there can still be a driving force for the reaction.

Thermodynamic stabilities depend mainly on the strength of the bonds from metal to carbon. They can be estimated by bond enthalpy (\( \bar{E}_b \) \( \text{M} - \text{C} \)) measurements; compounds with strong \( \text{M} - \text{C} \) bonds are, not surprisingly, more stable than those with weaker \( \text{M} - \text{C} \) bonds. Although not inherently weak, \( \text{M} - \text{C} \) bonds are less strong than \( \text{M} - \text{N} \), \( \text{M} - \text{O} \) and \( \text{M} - \text{X} = \text{halogen} \) bonds. (Table 1.1). Free energies of formation (\( \Delta G^\circ \)) are not usually known for organometallics as standard entropies are rarely known and so enthalpies of formation (\( \Delta H^\circ \)) are usually used in comparing thermodynamic stabilities. Hence organometallic reactions are exothermic or endothermic (\( \Delta H^\circ \) is negative or positive), but free energies (\( \Delta G^\circ \)) are not known other than that they are negative and hence, in a formal sense, neither are thermodynamic stabilities. For alkyl organometallics mean bond enthalpies for the whole molecule (\( \bar{E} \ (\text{M} - \text{C}) \)) are usually quoted, but there is a problem here in that stepwise bond dissociation energies (\( D_1 - D_n \)) may deviate a lot from the mean values, viz

\[
\bar{E} = \frac{1}{n} \sum_{i=1}^{n} D_1.
\]

(see \( \text{Me}_2\text{Hg} \) below, Equation 1.2, 1.3)

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{Hg} & \rightarrow \text{CH}_3\text{Hg} + \text{CH}_3 & D_1(\text{Hg} - \text{C}) = 214\text{kJ mol}^{-1} & \text{(1.2)} \\
\text{CH}_3\text{Hg} & \rightarrow \text{Hg} + \text{CH}_3 & D_2(\text{Hg} - \text{C}) = 29\text{kJ mol}^{-1} & \text{(1.3)}
\end{align*}
\]
Thermodynamic Stabilities of Organometallic Compounds

Table 1.1  Bond dissociation energies\(^a\) of diatomic molecules (in kJ mol\(^{-1}\)). From Kerr JA, 1983, Strengths of chemical bonds, *Handbook of Chemistry and Physics*, Chemical Rubber Company, 65 edn, F171–181 Reprinted with permission. Copyright CRC Press Inc, Boca Raton, Fla, USA

<table>
<thead>
<tr>
<th>Main group elements(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Ga</td>
</tr>
<tr>
<td>Ln</td>
</tr>
<tr>
<td>Tl</td>
</tr>
</tbody>
</table>

\(^{a}\) D(M—X) = M\(^+\) + X\(^-\), i.e. bond dissociation enthalpy; loosely, bond strength

\(^{b}\) In kJ mol\(^{-1}\) measured spectroscopically (mass spectrum) from transient molecules as above, at 25 °C

Hence \(\bar{E} = 121.5\ \text{KJ mol}\(^{-1}\)\), but this does not reflect the difficulty of breaking the *first* Hg—C bond [6].

What matters here is that some organometallic compounds are exothermic towards decomposition to their elements, and some are endothermic, but not all of the exothermic compounds decompose (kinetics again!). Also, when they do decompose on heating they usually do so to a mixture of hydrocarbons, hydrogen and the metal, not to the elements. Nevertheless, quantification information from such measurements is a useful guideline and, is usually all that is available. Data is given in Tables 1.2 to 1.4.

The information in the tables relates to decomposition to the elements in their standard states, but this is not what usually happens. Taking (CH\(_3\))\(_4\)Pb for example (Table 1.5) it can be seen that there are other routes than those to elements. On this basis route 4 is apparently the most favoured.

Despite the apparent thermodynamics (we don’t know the entropy values), (CH\(_3\))\(_4\)Pb is an important, readily available and commercial compound. The reason is, again, kinetic stability. The reaction pathway at room temperature does not have an activation energy low enough for it to happen at a measurable rate. The activation energy in such cases may depend on the inherent M—C bond strength and this appears to be strong enough to allow (CH\(_3\))\(_4\)Pb stored in an inert atmosphere to be indefinitely stable.

In practice, in the environment, decay mediated by oxygen, water, free radicals and biology is much more relevant. Many kinetically stable organometallics in these terms may be very unstable in the environment, including (CH\(_3\))\(_4\)Pb which decays in days in the atmosphere (Chapter 4).

So while all carbon compounds (including organometallics) are thermodynamically unstable owing to the stability of the products (again assuming entropy values), many are kinetically stable because there is no low energy route to decomposition. This may be associated with there being a closed shell of electrons, often of spherical symmetry, around the metal atoms, i.e. full use of
Table 1.2  Standard enthalpies of formation $\Delta H^0_\circ$ (kJ mol$^{-1}$) and mean bond enthalpies, $\bar{E}$ (M–C) (kJ mol$^{-1}$) of CH$_3$ derivatives in the gas phase$^a$

<table>
<thead>
<tr>
<th>MMe$_2$</th>
<th>MMe$_3$</th>
<th>MMe$_4$</th>
<th>MMe$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>$\Delta H^0_\circ$</td>
<td>$\bar{E}$</td>
<td>M</td>
</tr>
<tr>
<td>Zn</td>
<td>50</td>
<td>177</td>
<td>B</td>
</tr>
<tr>
<td>Cd</td>
<td>106</td>
<td>139</td>
<td>Al</td>
</tr>
<tr>
<td>Hg</td>
<td>94</td>
<td>121</td>
<td>Ga</td>
</tr>
<tr>
<td>Tl</td>
<td>—</td>
<td>—</td>
<td>Sn</td>
</tr>
</tbody>
</table>

$^a$ mean 'bond strengths'. $n\bar{E}$(M–CH$_3$) = $\Delta H^0_\circ$(M(g)) + $n\Delta H^0_\circ$(CH$_3$) - $\Delta H^0_\circ$(M(CH$_3$)$_n$(g))

Notes:
(i) Some compounds are exothermic, some are endothermic with respect to decomposition to elements n the absence of air/water.
(ii) $\bar{E}$ (M–C) decreases with increasing atomic number for main group elements (it is the opposite for transition metal–metal compounds) due to increasing orbital dimensions on M and poorer covalent overlap.
(iii) These bonds are weak compared to metal–oxygen, metal–halogen, carbon–oxygen bonds in weakness of organometallic to oxidation.
(iv) Mean bond enthalpies can be misleading (see text).
(v) Analogous values of $\bar{E}$ for some transition metal carbonyls are Cr(CO)$_5$, $\bar{E}$ = 107; Mo(CO)$_5$, $\bar{E}$ = 152; W(CO)$_5$, $\bar{E}$ = 180. Note increasing bond strength down the group.
(vi) Mode of decomposition is via homolytic breakage of the M–C bond to produce radical species.

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Table 1.3  $E^0_{298}$ Values for the first M–C bond in some polyatomic molecules (kJ mol$^{-1}$)

<table>
<thead>
<tr>
<th>M</th>
<th>$E^0_{298}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$–Ge(CH$_3$)$_3$</td>
<td>346 ± 17</td>
</tr>
<tr>
<td>CH$_3$–Sn(CH$_3$)$_3$</td>
<td>297 ± 17</td>
</tr>
<tr>
<td>CH–Pb(CH$_3$)$_3$</td>
<td>238 ± 17</td>
</tr>
<tr>
<td>CH$_3$–As(CH$_3$)$_2$</td>
<td>280 ± 17</td>
</tr>
<tr>
<td>CH$_3$–Sb(CH$_3$)$_2$</td>
<td>255 ± 17</td>
</tr>
<tr>
<td>CH$_3$–Bi(CH$_3$)$_2$</td>
<td>218 ± 17</td>
</tr>
<tr>
<td>CH$_3$–CdCH$_3$</td>
<td>251 ± 17</td>
</tr>
<tr>
<td>CH$_3$–HgCH$_3$</td>
<td>255 ± 17</td>
</tr>
<tr>
<td>CH$_3$–SH</td>
<td>312 ± 4.2</td>
</tr>
<tr>
<td>CH$_3$–SCH$_3$</td>
<td>272 ± 3.8</td>
</tr>
</tbody>
</table>

Notes:
(i) Compare with Table 1.2. The above bonds are $>\bar{E}$ (M–C).
(ii) Measurement of bond strengths in polyatomic molecules is not straightforward, being hard to measure (usually by kinetic methods). Some can be calculated at 298 K from the following equation:

$$E^0(R–X) = \Delta_H^0(R) + \Delta_H^0(X) - \Delta_H^0(RX)$$

or

$$E^0(R–R) = 2\Delta_H^0(R) - \Delta_H^0(R–R)$$

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Table 1.4  Mean bond enthalpies ($\bar{E}$ (M–C)) for oxides and halides

<table>
<thead>
<tr>
<th>M</th>
<th>$\bar{E}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B–O</td>
<td>526</td>
</tr>
<tr>
<td>B–Cl</td>
<td>456</td>
</tr>
<tr>
<td>Al–O</td>
<td>500</td>
</tr>
<tr>
<td>Al–Cl</td>
<td>420</td>
</tr>
<tr>
<td>Si–O</td>
<td>452</td>
</tr>
<tr>
<td>Si–Cl</td>
<td>381</td>
</tr>
<tr>
<td>Si–F</td>
<td>565</td>
</tr>
<tr>
<td>Sn–Cl</td>
<td>(tin)323</td>
</tr>
<tr>
<td>As–O</td>
<td>301</td>
</tr>
<tr>
<td>Bi–Cl</td>
<td>274</td>
</tr>
</tbody>
</table>

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Table 1.5 Decomposition of (CH$_3$)$_4$Pb

<table>
<thead>
<tr>
<th>Decomposition route</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta H$ per M—C$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Pb(CH$_3$)$_4(g)$ → Pb($s$) + 4C($s$) + 6H$_2(g)$</td>
<td>-136</td>
<td>-34</td>
</tr>
<tr>
<td>(2) Pb(CH$_3$)$_4(g)$ → Pb($s$) + 2C$_2$H$_4(g)$</td>
<td>-307</td>
<td>-76.75</td>
</tr>
<tr>
<td>(3) Pb(CH$_3$)$_4(g)$ → Pb($s$) + 2CH$_4(g)$ + C$_2$H$_4(g)$</td>
<td>-235</td>
<td>-58.75</td>
</tr>
<tr>
<td>(4) Pb(CH$_3$)$_4(g)$ → Pb($s$) + 2H$_2(g)$ + 2C$_2$H$_4(g)$</td>
<td>-33</td>
<td>-8.25</td>
</tr>
</tbody>
</table>

+kJ mol$^{-1}$

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the metal orbitals allowing no easy access to attacking reagents. Where available empty orbitals do exist, the compound may still be kinetically stable unless the metal–carbon (M—C) bonds are strongly polarized allowing, for example, nucleophilic attack by an external reagent.

Organometallics are also thermodynamically unstable with respect to oxidation to MO$_n$, H$_2$O and CO$_2$. Again kinetic reasons may render such compounds inert. Very reactive are compounds with free electron pairs, low-lying empty valence orbitals and highly polar M—C bonds.

We now consider kinetic stability for organometallic compounds.

1.5 KINETIC STABILITY OF ORGANOMETALLIC COMPOUNDS

In order to decompose, homolytic breakage of the M—C bond must first occur (Equation 1.4)

$$\text{MR}_{n+1} \rightarrow \text{MR}_n + \text{R} \quad (1.4)$$

In isolation this process is thermodynamically controlled by bond strengths (or enthalpies)—see above. However, once the short lived and reactive radicals are formed, further rapid reaction takes place to produce thermodynamically stable final products. None the less an energy input is required to break the metal–carbon bond. If the input is large (i.e. for a strong M—CH$_3$ bond) then a thermodynamically unstable compound ($\Delta G^\circ > 0$) may be stable at room temperature. The required energy input is known as the activation energy ($G^\ddagger$). This is illustrated in Figure 1.1.

However, even when $\Delta G^\circ$ is negative, $G^\ddagger$ may be large if the metal–carbon bond is strong. So thermodynamically unstable molecules may be kinetically stable, but when exposed to external attack, say by oxygen, water or microbes, they can soon decay. Strength of metal–carbon bonds is only a tendency towards environmental stability.

Some stability is dependent on molecular architecture other than metal–carbon bond strengths. Although many of the organometallics observed in the natural environment are metal methyls, others such as ethyleads and butyltins also exist and are observable in the environment. Organometallics
with metal alkyl groups other than methyl are susceptible to an important route to decomposition and on this ground alone should be less stable and less observed than metal methyls. This route is termed β elimination and occurs by migration of a hydrogen atom attached to a carbon atom at a remove of one other carbon atom from the metal (e.g. in an M—CH$_2$—CH$_3$ grouping but not limited to ethyl). The products are a metal hydride and ethenes (ethylene). That ethene is frequently observed in the natural environment may be related (Equation 1.5). Blockade of β elimination by alkyl groups not having a β hydrogen atom (e.g. —CH$_2$C(CH$_3$)$_3$, —CH$_2$CF$_3$, etc.) is not relevant to the environment.

$$CH_3CH_2MR_n^1 \rightleftharpoons HMR_n^1 \quad CH_2=CH_2$$ (1.5)

β elimination proceeds more rapidly down the groups in the periodic table because at the intermediate stage the metal is, in effect, increasing its coordination number. It may be assumed that β elimination could be involved (even when accompanied by hydroxide attack) in decay routes for compounds where decay is known to occur (e.g. butyltins) in compounds inputted into the environment, and why few ethyls and no higher alkyl species appear to be formed and stable in the environment. β elimination requires an empty valence metal orbital on M to interact with the electron pair on the C$_\beta$–H bond. Hence β elimination is more important for groups 1, 2 and 13 than for groups 14, 15 and 16. Empty orbitals can be blocked by ligands to increase stability. Two other processes are feasible but have never been investigated as environmental routes.
These are $\alpha$ hydrogen elimination (clearly possible with metal–methyl groupings) and orthometallation (where a nearby ortho aromatic hydrogen is transferred to the metal). Methyl and phenyl mercury species do decay in the environment and may do so by these routes. However in the presence of air, water and microbes, the above routes are likely to be minor ones.

1.6 STABILITY OF ORGANOMETALLIC COMPOUNDS TO ATMOSPHERIC OXIDATION

All organometallic compounds are thermodynamically unstable to oxidation because of the much lower free energy of the products of oxidation (metal oxide, carbon dioxide, water). Equation 1.6 gives an example.

$$(\text{CH}_3)_4\text{Sn(g)} + 8\text{O}_2 = \text{SnO}_{2(0)} + 4\text{CO}_{2(0)} + 6\text{H}_2\text{O}_{(g)}$$

$$\Delta H_m^0 = -3591 \text{ kJ mol}^{-1}$$

$$\Delta H_m^0 = \text{enthalpy change in reaction}$$

Here again, we rely on $\Delta H$ not $\Delta G$ values because of lack of knowledge of $\Delta S$; however, in view of the liberation of gaseous molecules, $T\Delta S$ will be an overall positive input into $\Delta G = \Delta H - T\Delta S$. This is very exothermic, but (CH$_3$)$_4$Sn is quite stable in air. Some, but not all, organometallic compounds however are spontaneously inflammable. Others, although thermodynamically unstable ((CH$_3$)$_4$Sn) still do not oxidize in this way for kinetic reasons, as discussed in Section 1.5 above. Interestingly and relevant, compounds which in bulk may spontaneously oxidize (burn; ignite) may be stable or decay much more slowly when they are attenuated (in dilute form, e.g. ppm or ppb in air). (CH$_3$)$_3$Sb has been noted in this respect.

Greater stability on attenuation follows from a consideration of the collision theory of gases. The rate constant is related to a collision number $Z$ (the number of reactant molecules colliding per unit time) and the activation energy $E$, the Arrhenius equation (Equation 1.7),

$$k = Z \exp (-E/RT)$$

where $k$ = rate constant, $E$ = activation energy, $R$ = gas constant and $T$ = absolute temperature.

$Z$ can be derived from classical gas kinetic theory as (Equation 1.8)

$$Z = \sigma_{AB}^2 \left[ \frac{8\pi k T m_A + m_B}{m_A m_B} \right]^{\frac{3}{2}} n_A n_B.$$
Occurrence and Pathways of Organometallic Compounds in the Environment

For these reasons, organometallics which, by their pyrophoric nature, alarm the laboratory chemist, may be much more stable in the environment.

The initial process of oxidation of organometallics by O\(_2\) is a rapid charge transfer interaction that occurs, involving electron donation from the organometallic to oxygen [11]. This is shown in Equations 1.9–1.11.

\[
\begin{align*}
R_nM + O_2 &\rightarrow R_nM^+O_2^- \\
R^0 + O_2 &\rightarrow RO^0_2 \\
RO^0_2 + R_nM &\rightarrow RO_2R_{n-1}M^0 + R^0
\end{align*}
\]

(1.9) \hspace{1cm} (1.10) \hspace{1cm} (1.11)

The species \(R_nM^+O_2^-\) may decay by various routes, and peroxides may be formed or coupling of the alkyl ligands may occur. Organocarbon and -mercury compounds are oxidized by radical chain SH\(_2\) processes as exemplified below, following the initial charge transfer processes, (Equations 1.12 and 1.13); [11]

\[
R_3B + RO^0_2 \rightarrow R_2BOOR + R^0
\]

(1.12)

\[
R^0 + O_2 \rightarrow RO^0_2, \text{ etc}
\]

(1.13)

The comparative susceptibilities of some metal–carbon bonds to oxidation to metal oxides are demonstrated in Tables 1.6 and 1.7. For main group elements they suggest increasing liability to oxidation as the group is descended.

Atmospheric oxidation will tend to occur rapidly:

(i) Where metal–carbon bonds are very polar, the partial charges on \(M(\delta +)\) or \(C(\delta -)\) may facilitate attack by external reagents including oxygen. This can be observed indirectly by considering electronegativity values (Table 1.8). Electronegativity is the ability of an atom in a molecule to attract a shared

| Table 1.6 | Comparative bond enthalpy terms for metal–carbon and metal–oxygen bonds\(^a\) (in kJ mol\(^{-1}\)). Data gives an assessment of comparative bond strengths. (Reproduced with permission Johnson DA 1982 Some Thermodynamic Aspects of Inorganic Chemistry (2nd edn). Cambridge University Press, pp 201–2). |
|-----------|----------------------------------|----------------------------------|----------------------------------|
| Group 14  | M—C | M—O | Group 15 | M—C | M—O | Group 16 | M—C | M—O |
| C         | 347 | 358 | N       | 314 | 214 | O       | 358 | 144 |
| Si        | 320 | 466 | P       | 276 | 360 | S       | 289 | 522(S—O) |
| Ge        | 247 | 385 | As      | 230 | 326 | Se      | 247 |
| Sn        | 218 | 218 | Sb      | 218 |
| Pb        | 155 | 141 | Bi      | 141 |

\(\begin{align*}
B—C &\ = \ 364 \\
B—O &\ = \ 520
\end{align*}\)

\(\begin{align*}
C—H &\ = \ 413 \\
O—H &\ = \ 464 \\
N—H &\ = \ 391 \\
H—H &\ = \ 436 \\
C—Cl &\ = \ 346 \\
\end{align*}\)

\(a\) From thermodynamic data on the decomposition of the molecules, e.g. \(C_2H_6\). Calculated from thermodynamic cycles

Definitions as in Table 1.3. \(M = \) elements listed
### Table 1.7 Stability of methylmetals to oxygen$^a$

<table>
<thead>
<tr>
<th>Stable</th>
<th>Unstable$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$)$_2$Hg</td>
<td>CH$_3$PbX$_3$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$Si, [(CH$_3$)$_2$SiO]$_n$, (CH$_3$)$_3$Si$^{(4-n)+}$, (CH$_3$)$_3$Si$_2$</td>
<td>CH$_3$Ti$^+$</td>
</tr>
<tr>
<td>(CH$_3$)$_4$Ge, (CH$_3$)$_4$Ge$^{(4-n)+}$, (CH$_3$)$_4$Ge$_2$</td>
<td>(CH$_3$)$_2$Zn(CH$_3$Zn$^+$ also)</td>
</tr>
<tr>
<td>(CH$_3$)$_4$Sn</td>
<td>(CH$_3$)$_2$Cd(CH$_3$Cd$^+$ also)</td>
</tr>
<tr>
<td>(CH$_3$)$_4$Pb$^-$</td>
<td>(CH$_3$)$_3$B</td>
</tr>
<tr>
<td>CH$_3$HgX(C$_6$H$_5$ and C$_2$H$_5$ also stable)</td>
<td>(CH$_3$)$_4$Al</td>
</tr>
<tr>
<td>(CH$_3$)$_4$SnX$_n$</td>
<td>(CH$_3$)$_2$Ga</td>
</tr>
<tr>
<td>(CH$_3$)$_3$PbX</td>
<td>(CH$_3$)$_2$In</td>
</tr>
<tr>
<td>(CH$_3$)$_2$PbX$_2$</td>
<td>(CH$_3$)$_2$Tl</td>
</tr>
<tr>
<td>(\pi(CH_3)_2C_3H_2Mn(CO)_3^c)</td>
<td>(CH$_3$)$_5$As</td>
</tr>
<tr>
<td>CH$_3$Mn(CO)$_2$L$^d$</td>
<td>(CH$_3$)$_3$As$^e$</td>
</tr>
<tr>
<td>(CH$_3$)$_2$AsO(OH)</td>
<td>(CH$_3$)$_2$Sb$^e$</td>
</tr>
<tr>
<td>CH$_3$As(O)(OH)$_2$</td>
<td>(CH$_3$)$_3$Bi</td>
</tr>
<tr>
<td>(CH$_3$)$_2$S</td>
<td>(CH$_3$)$_2$AsH</td>
</tr>
<tr>
<td>(CH$_3$)$_3$Se</td>
<td>CH$_3$AsX$_2$</td>
</tr>
<tr>
<td>CH$_3$HgSeCH$_3$</td>
<td>CH$_3$SbX$_2$</td>
</tr>
<tr>
<td>CH$_3$COB$_2$(solid state)</td>
<td>(CH$_3$)$_4$SnH$_n$$^e$</td>
</tr>
<tr>
<td>(CH$_3$)$_2$SbO</td>
<td>(CH$_3$)$_6$Sn$_2$(At RT gives [(CH$_3$)$_3$Sn]$_2$O)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$SbO(OH)</td>
<td>(CH$_3$)$_6$Pb$_2$(to methyl lead products)</td>
</tr>
<tr>
<td>CH$_3$SbO(OH)$_2$</td>
<td>(CH$_3$)$_2$Sb</td>
</tr>
<tr>
<td>(CH$_3$)$_2$Ti$^{+}$, (CH$_3$)$_2$Ga$^+$</td>
<td>(CH$_3$)$_2$AsO</td>
</tr>
<tr>
<td>(CH$_3$)$_3$S$^+$</td>
<td>(CH$_3$)$_2$P</td>
</tr>
<tr>
<td>(CH$_3$)$_3$Se$^+$</td>
<td>(CH$_3$)$_4$SiH$_4$-n</td>
</tr>
<tr>
<td>(CH$_3$)$_3$PO</td>
<td>(CH$_3$)$_4$GeH$_4$-n</td>
</tr>
</tbody>
</table>

$^a$ At room temperature in bulk (assume similar but lesser environmental stability for ethyls). As against rapid (seconds, minutes) oxidation. Table to be read in conjunction with Table 1.6. Not necessarily stable against water (see Table 1.9).

$^b$ Variousy unstable because of empty low lying orbitals on the metal, polar metal–carbon bonds and/or lone electron pairs on the metal.

$^c$ Gasoline additive.

$^d$ To exemplify ligand-complexed transition metal organometallics. Many of these synthetic compounds are oxygen stable but none have been found in the natural environment.

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$^e$ But stable in dilute form and detected in the environment (Ch.3).

(ii) electron pair to itself, forming a polar covalent bond. The values of electronegativity computed by Pauling (Table 1.8) still remain the best indicator of polarity, as dipole moments apply to the molecular as a whole, not just to the bond (whose dipole may therefore only be estimated indirectly).

(ii) Where empty low lying (valence) orbitals on the metal exist, or where the metal has a lone electron pair (non-bonding pair), then this also facilitates kinetic instability to oxidation. The oxygen molecule (a diradical) can attack empty orbitals on M, e.g. d orbitals.

(iii) Where the compound is thermally (thermodynamically) unstable anyway.

(iv) Where full coordination complexation with stabilizing ligands is not occurring.
Table 1.8  Some electronegativity values relative to carbon

<table>
<thead>
<tr>
<th>Group 13</th>
<th>Group 14</th>
<th>Group 15</th>
<th>Group 16</th>
<th>Group 17</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>2.0</td>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>Al</td>
<td>1.5</td>
<td>Si</td>
<td>1.8</td>
<td>P</td>
</tr>
<tr>
<td>Ga</td>
<td>1.6</td>
<td>Ge</td>
<td>1.8</td>
<td>As</td>
</tr>
<tr>
<td>Ln</td>
<td>1.7</td>
<td>Sn</td>
<td>1.8</td>
<td>Sb</td>
</tr>
<tr>
<td>Tl</td>
<td>1.8</td>
<td>Pb</td>
<td>1.8</td>
<td>Bi</td>
</tr>
</tbody>
</table>

Notes
1. The C—S bond is non-polar. The electrons are distributed midway between C and S.
2. For the other environmental main group elements (E) the electrons are closer in the covalent bond to carbon (i.e. $M^8_-—C^8-$).

Conversely complexation requires available empty orbitals on the metal. It is a competition between available ligands and atmospheric oxygen. $(CH_3)_4Sn$ is quite stable in air (fully coordinated) whereas $(CH_3)_2Zn$ is pyrophoric (empty orbitals, coordinatively unsaturated).

1.7 STABILITY OF ORGANO METALLICS TO WATER

The first step in the hydrolysis of an organometallic compound is usually nucleophile attack of the lone electron pair on the water oxygen atom to an empty metal orbital on the organometallic. Hence hydrolytic instability is also connected with empty low-lying orbitals on the metal and on the ability to expand the metal coordination number. The rate of hydrolysis is connected with the polarity of the metal–carbon bond; strongly polarized $(M^8_-—C^8-)$ bonds are unstable to water. These are found for example in groups I and II organometallics and for those of zinc and cadmium. The influence of polarity is shown for alkylboron compounds which have low polarity and are water stable although unstable to air. Low polarity compounds which cannot easily expand their coordination number are expected to be water stable. Most metal alkyls and aryls are thermodynamically unstable to hydrolysis to metal hydroxide and hydrocarbon (Equation 1.14). Many, though, are kinetically stable. Examples are given in Table 1.9.

$$R_nM + nH_2O \rightarrow M(OH)_n + nRH \quad (1.14)$$

To illustrate, SiCl$_4$ is easily attacked by water, owing to the low lying 3d orbitals on silicon being polarized ($\delta^+$) by the electron attracting chloride ligands. $(CH_3)_4Si$ is kinetically inert to hydrolysis at room temperature because the Si—C bonds are less polarized than the Si—Cl bonds.
Table 1.9  Stability of organometallic species to water

<table>
<thead>
<tr>
<th>Organometallic</th>
<th>Stability, comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂Hg, R₄Sn, R₄Pb</td>
<td>Only slightly soluble, stable, diffuse to atmosphere. Higher alkyls less stable and less volatile. Species generally hydrophobic and variously volatile</td>
</tr>
<tr>
<td>CH₃HgX, (CH₃)₄Sn(₄₋ₙ)⁺</td>
<td>Stable, slightly soluble depending on X. Soluble, methyltin units stable but made hexa- and penta-coordinate by H₂O, OH⁻. Species are solvated, partly hydrolysed to various hydroxo species. At high pH polynuclear bridged hydroxo species form for (CH₃)₃Sn²⁺</td>
</tr>
<tr>
<td>(CH₃)₂Pb⁺</td>
<td>Soluble, hydrolysis as methyltins above. Also dismutates to (CH₃)₂Pb and (CH₃)₂Pb²⁺ at 20 °C</td>
</tr>
<tr>
<td>(CH₃)₂Pb²⁺</td>
<td>Soluble as for (CH₃)₂Pb⁺ above. Disproportionates to (CH₃)₃Pb⁺ and CH₄ slowly. These reactions cause eventual total loss of (CH₃)₂Pb⁺ and (CH₃)₂Pb²⁺ from water.</td>
</tr>
<tr>
<td>(CH₃)₂As⁺</td>
<td>Hydrolyzes to (CH₃)₂AsOH then to slightly soluble [(CH₃)₂As]₂O</td>
</tr>
<tr>
<td>CH₃As³⁺</td>
<td>Hydrolyzes to CH₃As(OH)₃, then to soluble (CH₃AsO)₃</td>
</tr>
<tr>
<td>CH₃₂AsO(OH)</td>
<td>Stable and soluble (330 g dm⁻³). Acidic pKₐ = 6.27, i.e. cacodylic acid, dimethylyarsonic acid. Detected in oceans</td>
</tr>
<tr>
<td>CH₃AsO(OH)₂</td>
<td>Stable and soluble. Strong acid pK₁ = 3.6, pK₂ = 8.3—methylarsinic acid. Detected in oceans</td>
</tr>
<tr>
<td>(CH₃)₃S⁺, (CH₃)₃Se⁺, (CH₃)₃SiCl₄₋ₙ</td>
<td>Stable and slightly soluble</td>
</tr>
<tr>
<td>(CH₃)₃Ge(₄₋ₙ)⁺</td>
<td>Hydrolyse and condense but methylsilicon groupings retained</td>
</tr>
<tr>
<td>(CH₃)₂Ti⁺</td>
<td>Stable, soluble, have been discovered in oceans. Hydrolyse but (CH₃)n Ge moiety preserved</td>
</tr>
<tr>
<td>(CH₃)₃AsO, (CH₃)₃SbO</td>
<td>Very stable, soluble, but not been detected as a natural environment product</td>
</tr>
<tr>
<td>(CH₃)₃AsH, CH₃AsH₂</td>
<td>Insoluble, diffuse to atmosphere, air unstable</td>
</tr>
<tr>
<td>CH₃SbO(OH)</td>
<td>Stable and soluble. Detected in oceans</td>
</tr>
<tr>
<td>CH₃SbO(OH)₂</td>
<td>Stable and soluble. Detected in oceans</td>
</tr>
</tbody>
</table>

Other species
Stable and insoluble: R₃Si, (R₂SiO)ₙ, CH₃⋯H₂HgSeCH₃, most C₄H₃Hg derivatives, (CH₃)₂S, (CH₃)₂Se, (CH₃)₄Ge, (CH₃)₂B
Unstable: CH₃Pb⁺ (has not been detected in the environment), R₂Zn, R₂Cd, R₂Al, R₂Ga, (CH₃)₉Sn₂, (CH₃)₇Pb₂, (CH₃)₇Sb, CH₃Ti²⁺, CH₃Cd⁺, (CH₃)₉Sb⁺, CH₃Sb³⁺.
Solubility here refers to air-free distilled water, no complexing ligands. Range of solubilities is from mg dm⁻³ to g dm⁻³. Data from references.
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1.8 STABILITY OF ORGANOMETALICS TO LIGHT AND ATMOSPHERIC REAGENTS

The primary radiolytic decomposition process for organometallic compounds is electronic absorption leading to organic radical formation. The absorption may lead to d–d electronic transitions in the case of transition elements, or to charge transfer to or from metal orbitals. The former often causes the dissociation of
metal–ligand bonds, and hence coordinative unsaturation, and the latter may facilitate nucleophilic attack at the metal. For organometallic compounds photo properties are more dependent on the wavelength of excitation radiation than is the case for organic compounds. Light stability is more relevant for volatile, i.e. \( R_nM \), species as it is they that enter the atmosphere, and not the organometallic cationic derivatives that are complexed in sediments, water, etc. The most important of these are \((\text{CH}_3)_2\text{Hg}, \text{R}_4\text{Pb}, \text{R}_4\text{Sn}, (\text{CH}_3)_3\text{As}, (\text{CH}_3)_3\text{Sb}, \text{and (CH}_3)_2\text{Se}\).

Photoysis of \((\text{CH}_3)_2\text{Hg}\) at 254 nm in the gas phase produces \(\text{CH}_3\text{Hg}^0\) and \(\text{CH}_3^0\) radicals, further reactions producing ethane and methane by hydrogen abstractions. At normal temperatures ethene is formed; methane occurs at higher temperatures. \(\text{CH}_3\text{HgI}\) in organic solvents at 313 nm forms \(\text{CH}_3^0\) by breaking of the mercury–carbon bond. In the gas phase, however, the mercury–halogen bond breaks. Diphenylmercury in organic solvents is photolysed to \(\text{C}_6\text{H}_5\) and also decomposes thermally [12].

Degradation of methyltin halides in water at about 200 nm was observed to produce inorganic tin via sequential degradation, [13] and irradiation of alkyllead compounds at 254 nm also leads to breakdown [14]. These wavelengths exist in the homosphere (see below) and hence these materials would be expected to decay if they volatilize to the atmosphere. Atmospheric fates are discussed in detail in the appropriate chapters.

Processes in the real atmosphere are more complex and, in general, lead to much reduced stability from that suggested by laboratory experiments. There is the additional presence of oxygen, other free radicals and surfaces on which enhanced decomposition will take place. Where this has been measured the lifetime of organometallics in the atmosphere may be in terms of hours or days, rather than years. The lifetime of \((\text{CH}_3)_4\text{Pb}\) in the atmosphere, for example, has been estimated as several days [15].

From Figure 1.2, laboratory processes using wavelengths shorter than 340 nm might be thought to be less relevant under normal conditions for the lower atmosphere as radiation of these wavelengths hardly penetrates to the earth’s surface [16]. However, at up to 85 km the atmosphere is homogeneous (homosphere) [17] and volatile materials released into it will, if stable, eventually circulate to that height and be subject to interaction with radiation penetrating to levels below 85 km. A wavelength of 120 nm is equivalent to 998 kJ mol\(^{-1}\); 240 nm is equivalent to 499 kJ mol\(^{-1}\) and 340 nm equals 352 kJ mol\(^{-1}\). These are generally sufficient to homolyse metal–carbon bonds. The main absorbing medium at wavelengths below 340 nm is ozone, whose importance to biology is clear in view of the toxicity of short wavelength radiation. It might, therefore, be inferred that \((\text{CH}_3)_2\text{Hg}, \text{R}_4\text{Pb} \text{and } \text{R}_4\text{Sn}, \text{etc. will photolysed in the atmosphere to methyl radicals and } (\text{CH}_3)_n\text{M}^0\), and that further reactions to produce methane, ethane and other hydrocarbons will occur. However this is not the main decomposition process.

In addition to direct photolysis, reactions with other species produced by atmospheric photochemistry will also occur (e.g. \(\text{OH}^*, \text{O}_3^3\text{P} \text{and } \text{O}_3\)). These
Figure 1.2  Absorption of light in the atmosphere
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occur faster than alternative heterogeneous processes available after adsorption on particles. \((\text{CH}_3)_4\text{Pb}\) has been most thoroughly investigated [18] from this point of view (details are given in Chapter 4) but hydroxyl radical attack seems to be the most important first step reaction [19] here, viz. Equations (1.15–1.17). These chemical decomposition routes are much faster, in fact, than the photolytic decomposition processes described above when the real atmosphere is considered.

\[
(\text{CH}_3)_4\text{Pb} + \text{OH}^0 \longrightarrow (\text{CH}_3)_3\text{PbCH}_2^0 + \text{H}_2\text{O} \quad (1.15)
\]

\[
(\text{CH}_3)_4\text{Pb} + \text{O}_3 \longrightarrow (\text{CH}_3)_3\text{PbOOH} + \text{CH}_2\text{O} \quad (1.16)
\]

\[
(\text{CH}_3)_4\text{Pb} + \text{O}^3\text{P} \longrightarrow (\text{CH}_3)_3\text{PbCH}_2^0 + \text{OH}^0 \quad (1.17)
\]

In view of these being reactions of a general nature, i.e. abstraction of hydrogen from a methyl group; insertion of ozone into a metal–carbon bond, it is likely that other volatile organometallics are decomposed chemically in the atmosphere this way, and similar mechanisms are likely to exist for \(R_4\text{Sn}\), etc.

Thermal homolysis of metal alkyls leading initially to radical species \((\text{R}_n\text{M}^0 + \text{R}^0)\) produces the radicals in their ground energy states. Photolysis produces products in higher excited energy states and, therefore, more energy is required to decompose compounds than is needed by the thermal route.

Photochemistry is, however, more effective than thermal decomposition in promoting permanent decomposition as the excited product fragments are less likely to recombine. The energy required for photochemical dissociation varies
but for relevant organometallic molecules it will be of the order of 100–120 kJ mol\(^{-1}\) [20]. Taking \(D_1\) values (Table 1.10) for mercury, tin and lead, we should expect energies around 320, 370 and 300 kJ mol\(^{-1}\) to be required for the photochemical decompositions of \((\text{CH}_3\)\(_2\))Hg, \((\text{CH}_3\)\(_2\))Sn and \((\text{CH}_3\)\(_4\))Pb respectively. This is easily accomplished by, for example, 240 nm solar radiation (equivalent to 499 kJ mol\(^{-1}\)) which penetrates down to below 50 km altitude.

The volatile organometallics considered here are heavy molecules and their mixing ability in the atmosphere and consequent exposure to solar radiation must be considered. Higher diffusion into the atmosphere will give greater exposure to stronger intensities of radiation and faster photolysis. Higher energy radiation at greater height will also produced higher energy fragments, which are less likely to recombine. Mixing to cloud base level (varying from 0.5 to 12 km) is a rapid but complex phenomenon dependent on seasonal factors, temperature, inversions, maritime influence and the amount of atmospheric pollution in the area. Diffusion to greater heights is a slower process. For a fairly similar mass molecule \(	ext{CCl}_3\)F (MW 137.5 versus 178.7 for \((\text{CH}_3\)\(_4\))Sn), it has been calculated that 50 to 80 years elapse between the release of \(	ext{CCl}_3\)F at ground level and photochemical destruction at over 25 km altitude. (Boltzman distribution is assumed, leading to varied lifetimes for molecules.)

It can be concluded that the photochemical processes alone would decompose organometallics into radical species and the metals but that this might take decades. However, it should also be considered that other processes are occurring in the atmosphere, particularly where it is polluted. Atmospheric chemistry is complex. Species involved include \(\text{O}_3\), \(\text{O}\) (triplet\(^3\)P), \(\text{OH}^\circ\), \(\text{ClO}^\circ\), \(\text{HO}^\circ\), \(\text{NO}^\circ\). All of these are highly reactive radicals particularly able to abstract hydrogen atoms from hydrocarbons or organometallics. In addition, particle-based heterogeneous decomposition may occur. Radical or singlet oxygen attack on organometallic species in polluted atmospheres will actually decompose

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean bond enthalpy, (D^a)</th>
<th>(D_1)</th>
<th>(D_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3)(_2))\text{Hg}\</td>
<td>123</td>
<td>218</td>
<td>29</td>
</tr>
<tr>
<td>((\text{C}_2\text{H}_5))\text{Hg}\</td>
<td>101</td>
<td>179</td>
<td>25</td>
</tr>
<tr>
<td>((\text{iC}_3\text{H}_7))\text{Hg}\</td>
<td>88</td>
<td>113</td>
<td>63</td>
</tr>
<tr>
<td>((\text{CH}_3=\text{CH}))(_2)\text{Hg}\</td>
<td>141</td>
<td>202</td>
<td>80</td>
</tr>
<tr>
<td>\text{Hg}(\text{CN})(_2)\</td>
<td>302</td>
<td>517</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>252</td>
<td>97(^b)</td>
</tr>
<tr>
<td>((\text{CH}_3)(_4))\text{Sn}\</td>
<td>218</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)(_4))\text{Pb}\</td>
<td>155</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>((\text{CH}_3)(_2))\text{Zn}\</td>
<td>172</td>
<td>197</td>
<td>147(^c)</td>
</tr>
<tr>
<td>((\text{CH}_3)(_2))\text{Cd}\</td>
<td>141</td>
<td>189</td>
<td>92(^c)</td>
</tr>
</tbody>
</table>

\(^a\ D = \frac{D_1+D_2}{2}\ tec\)
\(^b\) Separate estimates
\(^c\) But note environmental instability despite \(D\) and \(D_1\) values compared to \((\text{CH}_3\)\(_2\))\text{Hg}

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these molecules rather than direct photochemical decomposition alone. It can be concluded that the lifetime of organometallic species in the atmosphere is of the order of hours or days rather than decades, with metals and hydrocarbons being produced. Actual measurements and estimates reinforce these conclusions (see, for example, Chapter 4).

Actual decay rates will vary widely and have been studied under environmental conditions, e.g. for lead where rates vary from 3 to 4% per hour in winter to 16 to 29% in summer for (CH$_3$)$_4$Pb [15, 18, 19]. For (C$_2$H$_5$)$_4$Pb the corresponding rates are 17–23 and 67–93%. These are upper limits but it can be seen that organometallics are not persistent in the atmosphere, with direct photolysis accounting for little of the decay. Even in the area of 340 nm radiation, where the atmosphere is fully transparent to light, the energy associated with the wavelength, (352 kJ mol$^{-1}$), is sufficient to break most metal–carbon bonds (Table 1.2) to produce ground energy state products. Shorter wavelengths are needed to produce higher energy state products, but normally chemical decomposition processes predominate [21].

For (CH$_3$)$_2$Hg also, a relatively fast degradation by hydroxyl attack has been deduced, with elemental mercury being produced and the rate constant for hydroxyl attack calculated at 2 × 10$^{11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ [22]. Overall it should be assumed that the common organometallic species emitted to atmosphere degrade rapidly and cannot be considered a serious environmental contaminant in most locations owing to their low concentrations (see relevant chapters) and relatively rapid rates of decay. The role and fate of their non-organometallic products merges into the field of organic and metallic atmospheric chemistry in general. That organometallics have a source and a transport role for metals in the atmosphere is clear.

1.9 COORDINATION PREFERENCES OF ORGANOMETALLIC SPECIES IN THE ENVIRONMENT

The general coordination preferences for metal cations has been understood by the Hard and Soft Acid and Base Principle. Hard acid metals are small, have higher oxidation states and are not easily polarized—they bond preferably to hard donor bases. Soft acid metals are larger, have lower oxidation states and are more polarizable, and prefer to coordinate to soft donor bases.

Inorganic metals in the environment tend to follow this principle—hard acid metals such as magnesium, calcium, tin(IV), etc. are found in the earth’s crust as oxides or carbonates, while softer metals such as mercury or lead are found in sulphides. Methyl groups are more electronegative than metals and generally withdraw electron density from metals (increasing hardness). Larger aliphatic groups are more electron releasing and polarizable than methyl groups and tend towards producing softer organometallic molecules overall, though the effect is small. Table 1.11 gives details.
Table 1.11  Hard and soft acids and bases

<table>
<thead>
<tr>
<th>Hard acids</th>
<th>Borderline acids</th>
<th>Soft acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₃As(3–n)+</td>
<td>(CH₃)₃Pb(4–n)+</td>
<td>CH₃Hg⁺</td>
</tr>
<tr>
<td>(CH₃)₃Ge(4–n)+</td>
<td>(CH₃)₃Sb(3–n)+</td>
<td>(CH₃)₃Ti(3–n)+</td>
</tr>
<tr>
<td>(CH₃)₃Sn(4–n)+</td>
<td>Rₙ Sn(4–n)+ (R &gt; CH₃)</td>
<td></td>
</tr>
</tbody>
</table>

Hard bases (ligands) include –NH₂, –OR, –OH, OA₂, Cl⁻ etc.; soft bases include higher alkyl groups, –SH, –SR, I⁻ etc. and so HgCH₃⁺ will be found bonded to sulphur where possible but chloride where necessary (sea water).

Taken from standard data in texts

Organometallic compounds in the aqueous and sediment environment will usually be stabilized by coordination to sediments and suspended particulate matter containing natural sulphur, by oxidation, or via nitrogen donor ligands which, by occupying coordination positions, will stabilize the metallic atom from attack. The fact that these ligands are often multitendate further increases stability owing to increased loss of entropy in the forward reaction and hence a more negative ΔG.

It should be pointed out that certain coordination reactions with oxygen and sulphur ligands [23–25] may, however, lead to labilization, not stabilization, through dismutation processes (see Chapters 2, 3 and 4). Examples are shown in Equations 1.18 and 1.19.

\[
2\text{CH₃Hg}⁺ + S²⁻ \rightarrow (\text{CH₃Hg})₂S \xrightarrow{Δ, hv} (\text{CH₃})₂Hg + HgS \quad (1.18)
\]

\[
6\text{(CH₃)}₃\text{Sn}⁺ + 3S²⁻ \rightarrow 3((\text{CH₃})₃\text{Sn})₂S \xrightarrow{Δ, hv} 3\text{(CH₃)}₄\text{Sn} + c((\text{CH₃})₂\text{SnS})₃ \quad (1.19)
\]

The driving force for these labilizations is the formation of stable products, e.g. HgS or c((CH₃)₂SnS)₃. In practice these processes have been shown to reduce the stability of the above organometallic species in the natural environment (see particularly Chapter 2), albeit increasing transport ability via the atmosphere.

1.10  STABILITY OF ORGANOMETALIC COMPOUNDS IN BIOLOGICAL SYSTEMS

Details of the toxicity and fate of organometallic compounds in organisms are given in the appropriate chapters. Where toxicity exists, numerous routes for breaking down organometallic species are available to organisms. These vary in rate; methylmercury has a half-life in man of about 70 days, triethyllead of around 35 days in one human compartment and 100 days in another. Half-lives vary between species and organisms but mechanisms for the decomposition of the metal–carbon bond do exist. There are several common routes linking decay processes for a variety of organometallics in various organisms.

Decay usually takes place by dealkylation. Methylmercury may be decomposed by numerous bacteria, first to methane and mercury(II), and finally to the
mercury(0) state. Arylmercury salts produce the arene and mercury(0). Full saturated tetramethyl organometallics (e.g. \((\text{CH}_3)_4\text{M}, \text{M} = \text{Sn, Pb}\)) are easily absorbed but rapid decay by loss of methyl group to the more stable trimethyl metal form takes place. For tetramethyllead, this conversion occurs rapidly in the liver—in rat liver there is a half-life of minutes. The trialkyls decay at various rates, eventually giving the metallic ions in various yields. In physiological saline, \((\text{CH}_3)_2\text{PbCl}_2\) is broken down to lead(II) with a half-life of about 12 days. Half-lives for methyl species are usually longer than for ethyl and higher alkyl analogues, owing to the presence in the latter of facile routes to decay [22]. The main route to dealkylation for higher alkyl metals, however, does not lie in direct metal–carbon bond cleavage but usually occurs after initial hydroxylation of the by the liver [23].

Enzymatic dealkylation of metals has been widely reported [24]. It occurs for example in the dealkylation of butyl- and cyclohexyltin compounds (Chapter 3) and in the decay of the ethyllead moiety (Chapter 4). Decay is usually reported at the β carbon but it also occurs at the α carbon; attachment at the metal may also occur, for example, in the case of silicon where the initial silanol product condenses to a silane. Phenyl groups do not usually undergo enzymatic hydroxylation but it is known for the phenylsilicon grouping [25].

For lower alkyl groups the organic products have been reported as alkanes and alkenes; for ethyllead species the product is reported to be ethanol. The gasoline additive \(\lambda\text{-CH}_3\text{C}_5\text{H}_4\text{Mn(CO)}_3\) is also attacked at the methyl position [26]. Hydroxylation is mainly carried out by liver microsomal monooxygenase enzyme systems [27]. From the above it can be seen that the importance of hydroxylation is the labilization it produces in the metal–carbon bond, allowing eventual dealkylation.

By contrast, it has been shown that organic arsenic compounds occurring naturally in seafood are transferred through the body with little change. The common organoarsenic compounds found in the environment, aquatic \((\text{CH}_3)_2\text{As(O)(OH)}\) and \(\text{CH}_3\text{AsO(OH)}_2\), are very stable against biological decay routes in plants and animals \((\text{CH}_3)_2\text{As}^+\text{CH}_2\text{COO}^-\) is also very stable. Soil bacteria have the ability to demethylate methylarsenic compounds, giving carbon dioxide by an oxidative route. A lack of arsenic demethylation in animals may be seen in the context of organoarsenic compounds being less toxic than their inorganic counterparts. The reverse is the case for most organometals (e.g. those of mercury, lead or tin).

### 1.11 GENERAL COMMENTS ON THE TOXICITIES OF ORGANOmetALLIC COMPOUNDS

The toxicities of the important environmental organometallic compounds are dealt with in the relevant chapters. There is also a detailed discussion of the
toxicity of organometallics and their interaction with living organisms in a recent book [28]. The toxicities of individual groups of organometallic compounds are separately discussed in a number of sources [29–32].

This section will present a brief summary of the main toxic mechanisms for environmental organometallics. In general, organometallic compounds are more toxic than the inorganic metal compounds from which they derive, often substantially so. Mercury, lead and tin obey this general rule, however, as noted, arsenic is an exception. Usually the toxic effects are at a maximum for the formal monopositive cations, i.e. the species derived by loss of one organic group from the neutral, fully saturated, organometallic, viz. $R_3\text{Pb}^+$, $R_3\text{Sn}^+$, $\text{CH}_3\text{Hg}^+$. It should be noted that the toxic effects of the saturated organometallics ($R_3\text{Sn}$, $R_4\text{Pb}$, etc.) usually derive from conversion to $R_3\text{M}^+$, etc., in organisms. In general alkyl groups are more toxic than aryl groups when attached to metals. The most toxic alkyl groups (attached to a common metal) vary from organism to organism, but methyl, ethyl and propyl groups tend to be the most toxic. For tin compounds toxicity of the organotin cations is at a maximum for the trialkyl series. For trialkyltins methyl and ethyl groups are the most toxic to mammals, with higher alkyl groups being more toxic to bacteria, invertebrates and fish; longer chain alkyl compounds are of lower toxicity to mammals.

Mechanisms of toxicity are varied, but good coordination to base atoms (e.g. S, O, N) on enzyme sites seems to be the main one. Coordination of the organometallic species (usually $R_n\text{M}^{n+}$) to the enzyme blocks the sites and prevents reaction with the biological substrate. Enzymes blocked in this way include lipoic acid (sulphur site), acetylcholinesterase (ester site) and aminolaeluvulinic acid dehydrase.

The other main result of organometallic introduction into vertebrates is a diminution of the myelin coating of nerve fibres. In addition, water accumulation and oedema in the central nervous system may occur. Other toxic effects are due to coordination to non-enzyme sites (e.g. thiols, histidine residues of proteins, haemoglobin, cytochrome $P_{450}$, cerebral receptors). Haematopoietic bone marrow, immune and essential trace metal systems in organisms may be affected by organometallic compounds. Fundamental interferences with DNA, protein synthesis, mutagenicity and genotoxicity have also been reported [33].

The reason for the enhanced toxicity of organometallics over the inorganic derivatives lies with the existence of lipophilic or hydrophobic groups (R) on the same species also having a hydrophilic dipole. This allows transport in aqueous body fluids, and also solubility and transport through fatty tissue and cell walls by diffusion. As Lewis acids (Table 1.11) similar to inorganic metal species, there is good bonding to Lewis base coordination sites within the organism (e.g. thiol groups).

The main result of organometallic poisoning in vertebrates is damage to the central nervous system, leading to varied symptoms including coma, ataxia, hyperactivity, varied motor difficulties, speech problems and psychological–attitudinal changes. Within the most prevalent series of environmental
organometallic compounds, triorganotin toxicity, for example, arises through disruption of calcium (Ca$^{2+}$) and mitochondrial functions, membrane damage, disruption of ion transport and inhibition of adenosine triphosphate (ATP) synthesis. Dialkyltins also inhibit oxygen uptake in mitochondria and inhibit α-ketoacid oxidation. Acute organic lead poisoning is chiefly focused on the central nervous system, with pathological changes to the brain being found, including neuron destruction and degeneration of nerve tracts. In general, serious but non-specific damage to the nervous system occurs in acute lead poisoning with organic lead compounds, with nerve cells in the hippocampus, reticular formation and cerebellum being particularly sensitive. At lower levels of poisoning incipient anaemia effects have been noted. Trialkyllead and -tin compounds, together with monomethylmercury, all bind to sulphydryl residues. Both trialkyllead and -tin compounds may destroy the normal pH gradient across mitochondrial membranes, thereby uncoupling oxidative phosphorylation.

The results of organomercury poisoning with respect to brain function are quite similar to those considered above. Rapid penetration of the blood–brain barrier leads to sensory disturbance, tremor, ataxia, visual and hearing difficulties. Methylmercury is lipid soluble, rapidly diffuses through cell membranes, and once it enters the cell is quickly bound by sulphydryl groups. It rapidly penetrates the blood–brain barrier. Methylmercury inhibits protein synthesis and RNA synthesis and causes particular damage to the developing brain.

A final general point is that the most subtle and early results of organometal poisoning cannot always be detected, particularly for lead and mercury. Here behavioural and psychological effects are shown and these are difficult to evaluate, especially in children. For instance, one of the earliest and most sensitive indices of methylmercury poisoning, paraesthesia, is very hard to measure and evaluate in children. In the case of lead, there is of course the debated and incompletely resolved case of low-level intellectual effects in children following (mainly) inorganic lead accumulation from organic lead gasoline additives. A particularly subtle effect of such cases is the difficulty in separating genuine toxic effects from other disease or socio-economic symptoms. These second level (or chronic) effects cause different problems in terms of evaluation and action than do acute high-concentration poisonings, and are an integral feature in the consideration of the environmental effects of organometallic compounds.

Discussion of the role of microorganisms in the oxidation, reduction and biomethylation of metals is discussed in greater detail in Section 1.13.

1.12 GENERAL CONSIDERATIONS ON ENVIRONMENTAL REACTIVITY OF ORGANOMETALLIC COMPOUNDS

A compound may be reactive if:

(i) the free energy of formation of products is negative,
(ii) the M—C bonds are polar,
(iii) the metal has empty low energy orbitals which a reagent may attack,
(iv) the metal has lone electron pairs (which may attach external environmental reagents or be used for coordination expansion),
(v) the metal—carbon bonds are weak (low bond energies),
(vi) the metal is coordinatively unsaturated, i.e. it can coordinate further ligands perhaps by using lone electron pairs. This coordinatively expanded species may be unstable, say, for steric reasons and lead to the decay of the entire assembly.
(vii) hydrogen atoms are present on the carbon atom \( \beta \) to the metal.

In general terms these effects produce low (activation) energy routes to decay.

1.13 MICROBIAL BIOTRANSFORMATION OF METALS AND METALLOIDS

1.13.1 INTRODUCTION

All microorganisms, whether prokaryotic\(^1\) or eukaryotic\(^2\), interact with the various classes of metals. The alkaline earth metals (Ca and Mg) have structural and catalytic functions, whereas some other metals (vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, tungsten) also have a catalytic function. The metalloid selenium is also known to have a catalytic function in certain microorganisms. In these roles, the concentrations of the elements required are very low and such interactions have biological rather than general environmental significance. Microorganisms can also transform metal and metalloid species by oxidation, reduction, methylation (alkylation) and demethylation (dealkylation). Many of these biotransformations have great environmental significance since changed chemical forms of metals can alter the physical and chemical properties, mobility and toxicity of an element. Some microbial biotransformations also have potential for bioremediation, e.g. of environmental sites contaminated with metal(loid)s.

In the following sections, some of the microbial transformations of metal (loid)s in each of four categories—reduction, oxidation, methylation and demethylation—are considered and summarized on an element by element basis. The intention is to illustrate the great diversity of metal(loid) biotransformations and their microbial catalysts. Where appropriate, comments relating to the physiological role, biochemical mechanism, environmental significance and bioremediation potential of the microbial biotransformations are included.

\(^{1}\) Microorganisms lacking a nucleus, and other membrane-enclosed organelles, i.e. bacteria and archaea.
\(^{2}\) Organisms with membrane-bound nucleus, such as fungi, algae and protozoa.
1.13.2 REDUCTION AND OXIDATION

In cellular respiration, electron transport occurs from a growth substrate (e.g. glucose) to an electron acceptor. In this process protons are pumped across a membrane to create a proton motive force, which is then used to drive cellular processes directly or to generate biologically useful energy in the form of adenosine triphosphate (ATP) (Figure 1.3). In eukaryotic microorganisms, such as fungi and algae, the electron acceptor molecule is oxygen and the process is termed aerobic respiration. Some fungi can also ferment—a process by which ATP is generated by substrate level phosphorylation—and this does not involve molecular oxygen. It is the prokaryotes (bacteria and archaea), however, that are well adapted to survival and growth in anaerobic environments, with anaerobic respiration being the major mode of ATP generation. In this mode of metabolism, a variety of inorganic and organic compounds may serve as alternatives to oxygen as terminal electron acceptors in respiration.

Only prokaryotes can use metal(loid)s as electron donors and conserve energy for growth from the oxidation. Similarly, it is only prokaryotes that have the capability of conserving energy for growth through reduction of metal(loid)s. In this role the metal(loid) serves as a terminal electron acceptor in anaerobic respiration, with energy being generated via coupling of an electron transfer chain to oxidative phosphorylation. Since relatively high concentrations of the metal(loid) are required to support microbial growth, either through oxidation or reduction, such transformation occurs on a large scale in the environment. For some microbial/metal(loid) interactions, oxidation or reduction of the metal (loid) occurs but the organism does not conserve energy from the transformation, i.e. it is not linked to growth. In many such cases, the transformations are thought to serve as a detoxification reaction for the metal (loid).

![Figure 1.3 Adenosine triphosphate (ATP)](image-url)
Several metal(loid)s are less soluble in the reduced state and microbial reduction can convert soluble metal(loid) species to insoluble forms that can more readily be removed, for example from contaminated waters. This offers the potential for bioremediation of metal(loid) contamination from polluted waters or waste streams. In the case of mercury, reduction of soluble Hg(II) forms volatile Hg(0), which is also regarded as a potential bioremediation strategy, albeit in a sense of transporting a problem elsewhere.

Some prokaryotes are also capable of producing volatile hydrides of metal (loid)s, such as arsine (AsH3) and stibine (SbH3). These transformations, although essentially bioreductions, will be considered alongside biomethylation since this process also generates volatile derivatives of metal(loid)s, including methyl hydrides.

We now consider redox reactions on an element by element basis, as the oxidation state of a metal is relevant to the stability and transport of its organometallic forms.

Chromium

A wide range of bacteria have been shown to reduce Cr(VI) to Cr(III) [34, 35] enzymatically, including the facultative anaerobe Enterbacter cloacae, the anaerobe Desulfovibrio vulgaris and a cyanobacterium [36]. The reduction is thought to be at least a two-step reaction involving Cr(V). Although chromium-reducing bacteria are widespread within the natural environment the extent of Cr(VI) reduction is determined largely by environmental factors, such as availability of electron donors, pH, redox conditions and temperature. Chromium bioreduction has potential for remediation of waters contaminated with Cr(VI) since Cr(III) is much less toxic [37]. Cr(III) also becomes immobilized in anaerobic sediments by adsorption [38], which can be viewed as a form of bioremediation.

A variety of carbon growth substrates have been shown to provide electrons for Cr(VI) reduction, including a range of sugars (e.g. glucose, mannose, sucrose, lactose), amino acids, aromatic compounds and fermentation end products such as acetate, butyrate and propionate [39–41]. The type of carbon substrate utilized is highly dependent upon both the nature of the organism and the prevailing aerobic/anaerobic growth conditions. In addition, D. vulgaris has been shown to reduce Cr(VI) under anaerobic conditions utilising hydrogen as the electron donor [42].

The rate of Cr(VI) reduction by microbial systems is influenced by the initial concentration of the ion, although differing trends have been observed. In the case of E. cloacae, high initial Cr(VI) concentrations showed relatively low rates of reduction [43, 44], whereas for E. coli the highest rates have been obtained at high Cr(VI) concentrations [45]. With regards to both pH and temperature, the highest rates of Cr(VI) reduction coincide with the optima for growth rate of...
the organisms [41, 43]. The influence of redox potential on Cr(VI) is also organism dependent. For *Bacillus* spp, Cr(VI) reduction has been shown to occur over a wide range of redox potentials from about +250 mV to −500 mV [46], whereas no reduction of Cr(VI) by *E. coli* occurs at initial redox potentials greater than −140 mV [47].

Cr(VI) bioreduction can occur under either aerobic or anaerobic conditions, or under both, depending upon the organism [34, 35, 44]. Under aerobic conditions, reduction of Cr(VI) occurs through the action of a soluble reductase protein, utilizing NADH as electron donor [42, 48]. Under anaerobic conditions, Cr(VI) is thought to serve as a terminal electron acceptor, with electrons being passed via a soluble and/or membrane reductase [42, 49]. Cytochromes are also thought to be involved; viz. cytochromes b and d in *E. coli* [48] and cytochrome c in *Enterobacter cloacae* [50]. There is no firm evidence, however, that electron transport to Cr(VI) is linked to energy generation (i.e. growth) [34]. The physiological role of Cr(VI) reduction to Cr(III) has not been established and may be a detoxification mechanism or a fortuitous reaction [51].

*Agrobacterium radiobacter* and *E. coli* have been shown to reduce chromium in liquid media under either aerobic or anaerobic conditions, although lower rates of Cr(VI) reduction are observed in the presence of oxygen [48]. Similarly, Cr(VI) reduction by *E. cloacae* under anaerobic conditions is lower in the presence of sulphate and nitrate; this inhibitory effect was not observed for *E. coli* [43, 45].

There appear to be no reports of microbial oxidation of Cr(III) to Cr(VI).

**Selenium**

Bacteria can reduce both SeO$_4^{2−}$ and SeO$_3^{2−}$ to Se(0), but only the former reduction has been shown to support growth [34]. SeO$_4^{2−}$-respiring bacteria are thought to be ubiquitous in the natural environment [52]. Dissimilatory SeO$_4^{2−}$ reduction has been reported to be inhibited by NO$_3$ but not by SO$_4^{2−}$, which suggests a role for nitrate reductase in dissimilatory selenium reduction [52]. However, the bacterium *Thauera selenatis* has been shown to grow anaerobically by reducing SeO$_4^{2−}$ via specific reductases that are distinct from those involved in NO$_3$ reduction [53–55]. Similarly, the facultatively anaerobic bacterium *Enterobacter cloacae* respires SeO$_4^{2−}$ under anaerobic conditions and reduces NO$_3$ concurrently [56, 57]. Washed cell suspensions of *E. cloacae* have also been shown to reduce SeO$_3^{2−}$, but this did not support growth. Interestingly, reduction of SeO$_3^{2−}$ by this organism is inhibited by nitrate and nitrite but *stimulated* by sulphate. Bacterial reduction of SeO$_3^{2−}$ to Se(0) is thought to be the major biological transformation for reduction of selenium in anaerobic sediment. Reduction of Se(0) to Se(II) (selenide) has been reported for *Thiobacillus ferrooxidans* [58].

1 Reactions that are directly or indirectly linked to energy formation but the element is *not* incorporated into biomass
Oxidation of Se(0) has been shown to occur in soils, although the organisms responsible have not been identified [59, 60]. Losi and Frankenberger [61] showed that the oxidation occurred at relatively slow rates, was mainly biotic in nature, and produced SeO$_3^{2-}$ alone or with SeO$_4^{2-}$. Oxidation of Se(0) by soils was enhanced by prior exposure to selenium. In liquid enrichment culture experiments, in the presence or absence of glucose or carbonate as carbon source, only SeO$_3^{2-}$ was detected as a product of Se(0) oxidation. Growth was detected in treatments containing Se(0) as the sole energy source, which suggests that some bacteria may conserve energy from the oxidation of selenium.

Uranium

Certain bacteria can grow by using U(VI) as a terminal electron acceptor in respiration, forming U(IV). Shewanella putrefaciens couples oxidation of hydrogen to U(VI) reduction, while Geobacter metallireducens uses acetate as electron donor [62]. Both bacteria are known iron reducers [63] and U(VI) is thought to replace Fe(III) as the terminal electron acceptor in respiration. Conversely, several Desulfovibrio species reduce U(VI) but this is not coupled to growth [64, 65], i.e. energy is not conserved in this reductive transformation. Cytochrome $c_3$ has been shown to be involved in U(VI) reduction by D. vulgaris [66].

Abdelouas et al. [67] have reported on the biocatalysed reduction of U(VI) in groundwater in the presence of high concentrations of nitrate, sulphate and carbonate. Microbially mediated reactions were sequential in order of decreasing redox potential, with U(VI) reduction accompanying that of sulfate and sulfide. U(VI) precipitated as a U(IV) solid adhering to bacteria.

Arsenic

Microbial reduction of arsenate (As (V) to arsenite As III) has been demonstrated for several bacterial genera [68], some of which are known to reduce arsenite further to form arsine or dimethylarsine (see Section 1.13.3). Micrococcus aerogenes and cell extracts of *M. lactilyticus* reduce arsenate to arsenite [69], while Methanobacterium strain MoH can reduce arsenate to dimethylarsine [70]. Certain Alcaligenes spp and Pseudomonas spp are known to reduce arsenate and arsenite to arsine (AsH$_3$) [71]. Since arsenate reduction in these strains has not been linked to growth, the physiological role of arsenate-to-arsenite reduction is likely to be detoxification only. Indeed, the only known means of microbial redox arsenate detoxification is reduction to arsenite followed by its expulsion. Studies on bacterial arsenate detoxification have mainly involved *Escherichia coli* and *Staphylococcus aureus*. The reductive detoxification enzymes (ArsC enzymes) are small (15 kDa molecular mass) monomeric protein being located in the cytosol$^1$ [72, 73]; the enzymes are
inducible\(^1\) and encoded by plasmid\(^8\) located genes [72, 74]. Reductive detoxification occurs in both aerobic and anaerobic environments, although the extent to which this mechanism contributes to overall arsenate reduction in relevant natural environments has not been estimated.

Arsenic respiration is now thought to be widespread in the environment and can be performed by diverse bacteria [75]. Bacteria from a reed bed [76], pristine freshwater and saline environments [77], surface sediments of a lake [78] and marsh-land [79] have been shown to grow by reducing arsenate. Isolated arsenic respirers include the Gram-positive Desulfotomaculum auripigmentum, capable also of respiring sulphate but not nitrate [80], and the Gram-negative Chrysiogenes arsenatis, capable of respiring nitrate but not sulphate [76].

Bacteria able to oxidize arsenite to arsenate have been isolated, including *Bacillus* and *Pseudomonas* spp [68]. The oxidation is thought to be a detoxification mechanism since bacteria are an order of magnitude more resistant to arsenate than to arsenite. Studies on a strain of Alcaligenes faecalis able to oxidize arsenite indicate that the transformation consumes oxygen, is induced by arsenite and does not yield utilizable energy [81]. Oxygen was shown to be the terminal electron acceptor, since respiratory inhibitors prevented further oxidation of arsenite. Heterotrophic bacteria are thought to play a major role in detoxifying the environment, catalysing up to 90% of arsenite transformation to arsenate [82].

**Mercury**

A variety of bacterial genera can reduce inorganic mercury (Hg(II)) to metallic mercury (Hg(0)), including *Cryptococcus*, *Pseudomonas*, *Staphylococcus* spp and a range of enteric bacteria [83–85]. The reduction occurs during aerobic growth and is thought to be a detoxification mechanism; the ability to reduce Hg(II) is often correlated with mercury resistance. The enzyme involved in mercury resistance—mercuric reductase (MR)—is a NADPH-dependent flavoprotein located in the cytosol [84, 86], which transfers two electrons to Hg(II) (Equation 1.20)

\[
\text{NADPH} + \text{RS-Hg-SR} + \text{H}^+ \rightarrow \text{NADP}^+ + \text{Hg(0)} + 2\text{RS}^-
\]  \hspace{1cm} (1.20)

Activity of the enzyme is enhanced by addition of thiols (R—SH) such as dithiothreitol and glutathione. The product Hg(0) is volatile and is released from the cell; it is much less toxic to the microorganism and to humans as compared to Hg(II).

Mercury resistance has been intensively studied in the bacterium *Pseudomonas aeruginosa*, where the genes for mercury resistance (*mer* genes) are located on a plasmid. The *mer* genes are arranged in an operon under the control of a regulatory protein. Hg(II) forms a complex with MerR, which activates

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\(^1\) Cellular content inside the cytoplasm, excluding membrane bound organelles.

\(^2\) Synthesis of enzymes stimulated by presence of ions/molecules (inducers) such as arsenate.

\(^3\) An extrachromosomal genetic element that is not essential for growth and has no extracellular form.
transcription of the mer operon, leading to synthesis of other Mer proteins, including mercuric reductase and a membrane transport protein for Hg(II). The role of the mer operon in Hg(II) resistance is illustrated in Figure 1.4.

Iron

Microbial dissimilatory reduction of Fe(III) to Fe(II) is thought to catalyse most Fe(III) reduction that occurs in sedimentary environments. A diverse range of bacterial genera have been associated with Fe(III) reduction, including Desulfovibrio, Desulfobacter, Geobacter, Aeromonas, Thiobacillus, Rhodobacter, Clostridium, Shewanella and Bacillus [87]. This form of anaerobic respiration can be coupled to the oxidation of a wide range of both organic (fatty acids, aromatic compounds, some amino acids) and inorganic electron donors [87], a feature arising from the high reduction potential of the Fe(III)/Fe(II) couple (0.77 mV). Since Fe(II) is a more soluble form of iron, dissimilatory bacterial reduction solubilizes iron from rocks and soils where Fe(III) is found as one of the most common metals.

A few bacteria can obtain energy from the oxidation of Fe(II) to Fe(III); the so-called ‘iron bacteria’ [88]. Since only a small amount of energy is conserved from this oxidation, the iron bacteria must oxidize large amounts of iron to grow and the ferric iron forms insoluble ferric hydroxide. Thiobacillus ferrooxidans is the best-known species and grows aerobically in acid mine drainage waters where the low pH stabilizes Fe(II) to chemical oxidation. Because the reduction potential of Fe(III)/Fe(II) is high (+0.77 V at pH 3) the path of electrons to oxygen is very short and the iron bacteria exploit the pre-existing proton gradients of their environment to generate ATP. The respiratory chain of T. ferrooxidans includes a copper-containing protein (rusticyanin) that accepts electrons from Fe(II) and donates electrons to membrane bound cytochrome c, with subsequent transfer via cytochrome a1 to oxygen. The natural proton motive force across the T. ferrooxidans membrane replenishes the protons used to reduce 0.5O2 via ATPase, generating ATP. Some aerobic iron-oxidizing bacteria—such as Gallionella ferruginea and Sphaerotilus natans—exist at near-neutral pH, but only at the interfaces between anoxic and oxic conditions where Fe(II) and O2 coexist. In entirely anoxicogenic environments Fe(II) is not oxidized abiotically at neutral pH, but can be oxidized by the purple bacteria. In these phototrophic bacteria, Fe(II) is used as an electron donor to reduce cytochrome c in the photosystem.

Manganese

Microorganisms able to reduce manganese are ubiquitous in the natural environment. They include fungi and both anaerobic and aerobic bacteria

---

1 A cluster of genes whose expression is controlled by a single operator.
Figure 1.4 Hg(II) reduction to Hg(0) in Pseudomonas aeruginosa. (a) The mer operon governing expression of Mer proteins. (b) Involvement of Mer proteins in transport and reduction of Hg(II).

* Area between the cytoplasmic membrane and the cell wall in certain (Gram negative) bacteria Adapted from Brock, *Biology of Microorganisms*, 9th edn, Madigan, M. T., Martinko, J. M., and Parker, J., Prentice Hall Int. Inc. with permission.

[89, 90]. Many different genera of bacteria have been shown to reduce manganese, including Pseudomonas, Bacillus, Corynebacterium and Acinetobacter [89].

Manganese can be reduced indirectly by spontaneous chemical reactions arising from bacterial metabolism. For example, manganese oxides are reduced by sulfur-reducing bacteria, such as Desulfovibrio spp, which generate sulfide as an end-product of dissimilatory sulfur reduction [91, 92]. Similarly, iron-
reducing bacteria can reduce Mn(IV) oxides through the formation of Fe(II) [93, 94]. Methane oxidation by methylotrophic bacteria is also coupled to manganese oxide reduction [95].

Direct enzymatic reduction of Mn(IV) by cell extracts of Acinetobacter calcoaceticus has been demonstrated [96], although involvement of an assimilatory nitrate reductase or a distinct Mn(IV) reductase has not been resolved. Dissimilatory Mn(IV) reduction is known to occur in certain facultatively anaerobic bacteria, such as Geobacter metallireductens [97]. In this process, manganese reduction is coupled to the oxidation of a non-fermentable carbon source (e.g. lactate), growth indicating that Mn(IV) serves as a terminal electron acceptor in anaerobic respiration. Inhibitors of electron transport have also been used to demonstrate the involvement of Mn(IV) in anaerobic respiration [89]. Studies using mutants lacking ferric and nitrate reductases demonstrate the involvement of a specific manganese reductase [90].

Various bacteria, algae and fungi oxidize Mn(II) [98]. The range of Mn(II) oxidizing bacteria is particularly diverse and includes common Gram-negative (e.g. Arthrobacter, Bacillus) and Gram-positive (e.g. Pseudomonas, Vibrio), sheathed bacteria (e.g. Lepothrix, Vibrio) and budding and appendaged bacteria (e.g Caulobacter, Pedomicrobium). Unequivocal evidence that bacteria can gain energy for growth through Mn(II) oxidation has not yet been obtained and the role of biotic Mn(II) oxidation is thought to be a protection against the toxicity of Mn(II) or that of the oxidant. Both indirect and direct mechanisms of manganese biooxidation are thought to exist. Indirect oxidation may occur through biological generation of hydrogen peroxide or oxygen free radicals [98, 99]. These indirect mechanisms of manganese oxidation are thought to protect aerobic bacteria, such as Leptothrix and Arthrobacter, from the toxic effects of strong oxidants produced during aerobic respiration. Direct oxidation of manganese involves binding of the element to oxidizing proteins. An intracellular protein is involved in Pseudomonas spp [100], whereas in Leptothrix spp [91] and Bacillus spp [101] an extracellular protein and a spore\(^\dagger\) protein have been implicated respectively. Other cellular components, such as the cell wall [102] and exopolysaccharides [103] are thought to be nucleating sites for manganese oxidation. Direct and indirect oxidation of soluble Mn(II) forms relatively insoluble Mn(III) or Mn(IV), which can precipitate around microbial cells.

1.13.3 METHYLATION AND ALKYLATION

Bioalkylation refers to the process whereby living organisms cause direct linkage of alkyl groups to metals or metalloids, thus forming metalloid–carbon bonds. The methyl group is the most common alkyl group transferred in a process termed biomethylation. This process has been extensively studied

\(^\dagger\) Resistant resting structure.
in nature and biomethylation activity has been found in soil, but mainly occurs in sediments from environmental waters such as estuaries, harbours, rivers, lakes and oceans. The attachment of a methyl group to a metalloid changes the chemical and physical properties of that element, which in turn influences toxicity, mobility and geological cycling. The organisms responsible for metalloid biomethylation are almost exclusively microorganisms. Anaerobic bacteria are thought to be the main agents of biomethylation in sediments and other anoxic environments. Some aerobic and facultatively anaerobic bacteria, as well as certain fungi and lower algae, have also been shown to be capable of metalloid biomethylation. With the exception of their cobalt content as vitamin B\textsubscript{12}, higher organisms do not seem to be capable of biomethylating true metals. The situation is different, however, for the metalloids arsenic, selenium and tellurium, and many higher organisms have been shown to form methyl derivatives of these elements, for instance methylarsenicals are formed in a wide range of organisms, including marine biota and mammals (including man).

Volatile methyl and hydride derivatives of metalloids have been found in gases released from natural and anthropogenic environments [104–107] (e.g. geothermal gases, sewage treatment plants, marine sediments, landfill deposits), and biological production of volatile compounds is thought to be a significant part of the biogeochemical cycles of metalloids such as arsenic, mercury, selenium and tin. With the exception of arsenic and selenium (and perhaps antimony), biomethylation increases toxicity because methyl derivatives are more lipophilic and therefore more biologically active.

Bioalkylation (the addition of a carbon bonded counter ion, e.g. riboside) is much rarer than biomethylation and has only been found for those metalloids capable of being biomethylated by higher organisms, i.e. arsenic, selenium and tellurium. Bioalkylation of arsenic has been studied most extensively and occurs mainly in marine species, with up to 96% of cellular arsenic being present in alkylarsenical (riboside) forms in certain algae. Conversion of inorganic arsenic to other arsenic–carbon containing organoarsenicals, such as arsenuolipids and arsenosugars, is thought to be a detoxification mechanism (see Chapter 5, Section 5.6). Bioalkylation may exist for mercury, lead, tin, etc., but no systematic search for a carbon containing counter ion has been made.

1.13.4 MECHANISMS OF BIOMETHYLATION

Biomethylation (i.e. methyl transfer) in organic molecules—such as proteins, nucleic acid bases, polysaccharides and fatty acids—occurs in all living cells and is an essential part of the normal intracellular metabolism. The three main biological methylating agents for organic molecules—\textit{S}-adenosylmethionine (SAM), methylcobalamine and \textit{N}-methylenetetrahydrofolate—have all been
shown to be involved in the biomethylation of metall(oids) (Figure 1.5). All three methylating agents have an extensive chemistry and have been studied intensively in relation to methylation of organic molecules. SAM is considered a 
ubiquitous methylating agent. It is synthesized by the transfer of an adenosyl 
group from ATP to the sulphur atom of methionine (Figure 1.6).

The positive charge on the sulphur atom activates the methyl group of 
methionine, making SAM a potent methyl carbonium ion donor. The methyl 
group in biochemistry is transferred as an intermediate radical (CH$_3^+$) or as a 
carbonium ion (CH$_3^+$) and thus the atom receiving the methyl group must be a 
nucleophile, which requires an available pair of electrons in the valency shell. In 
this oxidative addition process there is alternation of M$^{n+}$ and M$^{(n+2)+}$ oxidation 
states. The reaction is often referred to as the Challenger mechanism, after 
Frederick Challenger who first formulated it for methylation of arsenic [108, 
109] (see Figure 1.7 for the Challenger scheme). SAM has subsequently been 
also shown to be the methylating agent for the metall(oids) selenium, tellurium, 
phosphorus [110] and antimony [111], all of which have an available lone pair of 
electrons. N-Methyltetrahydrofolate (Figure 1.5), like SAM, is thought to 
transfer methyl groups as carbonium ions or as an intermediate radical, but 
its transfer potential is not as high as SAM. Conversely, for N-methylcobalamin 
(Figure 1.5)—a derivative of vitamin B$_{12}$—the methyl group is transferred as a 
carbanion (CH$_3$) and the recipient atoms must be electrophilic. Methylcobalamin 
is well established as a methylating agent for mercury and is also involved 
in methylation of lead, tin, palladium, platinum, gold and thallium [110]. 
Although methylcobalamin appears to be the sole carbanion-donating natural 
methylating agent, in the natural environment the carbanion can also be 
transferred to metals from other organometallic species that may be present, 
such as (CH$_3$)$_2$Pb$^+$ or (CH$_3$)$_2$Sn$^+$. Regardless of the methylating agent, only 
one methyl group is transferred to metal(oids) in each step, although further 
methyl groups may then be transferred to the same receiving atom.
Figure 1.5 Biological methylating agents involved in methylation of metall(oids). (a) S-Adenosylmethionine. (b) N-Methyltetrahydrofolate. (c) Methylcobalamin. The donated methyl groups are circled

**Mercury**

Biomethylation of mercury has been studied extensively. One reason for this is that methylation of mercury enhances lipid solubility and thus enhances bioaccumulation in living organisms. This has led to mercury entering the food chain and to severe mercury poisoning incidents, e.g. in Japan [112]. Many different bacteria in aerobic and anaerobic environments are known to catalyse mercury biomethylation, although anaerobic sediments are the main sites of environmental methylmercury formation [110]. Sulphur-reducing bacteria, such as *Desulfovibrio desulfituricans*, are thought to be the most important methylators of mercury [113–115]; both low pH and high sulfate concentrations promote mercury biomethylation activity within environmental sediments [116, 117].
As mentioned earlier, methylcobalamin is the methyl donor, giving rise to monomethylmercury and (in a slower step) dimethylmercury (volatile) products (Equations 1.21, 1.22).

\[
\text{CH}_3\text{CoB}_{12} + \text{Hg}^{2+} \rightarrow \text{CH}_3\text{Hg}^+ + \text{H}_2\text{OCO}_2\text{B}_{12}^+ \quad (1.21)
\]

\[
\text{CH}_3\text{CoB}_{12} + \text{CH}_3\text{Hg}^+ \rightarrow (\text{CH}_3)_2\text{Hg}^+ + \text{H}_2\text{OCO}_2\text{B}_{12}^+ \quad (1.22)
\]

Further reactions of methylmercury can occur via various abiotic mechanisms (e.g. disproportionation reaction involving H2S) also giving rise to dimethylmercury (see Section 1.9).
The key factor governing the concentration of mercury in biota is the concentration of methyl mercury in environmental waters, which is determined by the relative efficiencies of the methylation and demethylation processes. Methyl mercury in the environment is discussed in detail in Chapter 2.

**Arsenic**

A great diversity of microorganisms can methylate arsenic and in the natural environment methylarsenic compounds are widely produced, under both aerobic and anaerobic conditions [118]. The importance of fungal methylation of arsenic dates back to the second half of the nineteenth century, when several poisoning incidents in England and Germany were associated with arsenic-containing wall coverings. Gosio, in 1901, reported that a garlic-smelling, methylated arsenic compound was released from moulds growing in the presence of inorganic arsenic. Challenger and coworkers [108], in 1933, identified the gas as trimethylarsine ((CH₃)₃As). Several fungi have been shown to methylate arsenic under aerobic conditions, including filamentous *Scopulariopsis brevicaulis*, *Penicillium* spp, *Gliocladium roseum* and the yeast *Cryptococcus humicola* [109, 119, 120]. As mentioned earlier, the mechanism of arsenic methylation in fungi was established by Challenger [109] and involves a series of reductions and methylations, with SAM as methylating agent (Figure 1.7).

Certain bacteria have also been shown to methylate arsenic under aerobic conditions, including *Flavobacterium* spp, *Escherichia coli* and *Aeromonas* spp. Such bacteria-catalysed transformations can lead to di- and trimethylarsine derivatives, which have been widely found in environmental waters [121].

Arsenic biomethylation can also be catalysed by obligately anaerobic bacteria. *Methanobacterium* spp. can reduce AsO₃⁻ to AsO₂⁻, with subsequent methylation to methylarsonic acid, dimethylarsenic acid and dimethylarsine [121]. Methylcobalamin is the methyl donor for arsenic methylation by the methanogenic archaea [70]. Until recently, bacterial methylation of arsenic under anaerobic conditions was thought to stop at dimethylarsine ((CH₃)₂AsH) [121]. However, Michalke *et al.* [122] reported trimethylarsine in the gas phase above anaerobic cultures of *Methanobacterium formicicum*, *Clostridium collagogenovorans* and two *Desulfovibrio* spp. For *C. collagogenovorans* and *D. vulgaris*, trimethylarsine was the sole volatile arsenic species detected. Conversely, *M. formicicum* volatilized arsenic as mono-, di- and trimethylarsine and as arsine (AsH₃), while *Methanobacterium thermoautotrophicum* produced only arsine. These data serve to illustrate the high dependence of organism type on speciation of metal(loid) microbial transformations.

The biomethylation of arsenic is thought to serve as a detoxification process, since methylated forms of arsenic are far less toxic than arsenic(V) or its salts, etc. Further, methylation facilitates arsenic removal from living terrestrial organisms by excretion as water-soluble forms, such as methylarsonic acid
and cacodylic acid, or by volatilization as methylarsine derivatives [110, 121]. Higher animals, including mammals, are thought to be able to methyleate arsenic enzymatically [123], although the contribution from intestinal bacteria to formation of methylated arsenic compounds and thus to arsenic detoxification in higher animals is unclear. These aspects, and the extensive chemistry of natural product arsenoriboside in the marine and terrestrial environments, are discussed in Chapters 5 and 6.

**Antimony**

Mono- and dimethylantimony species have been found in both marine and terrestrial natural waters [124, 125]. Freshwater plants from two Canadian lakes influenced by mine effluent, and plant material from an abandoned antimony mine in the UK, have also been shown to contain methylantimony species [126, 127].

Biomethylation of inorganic antimony by the aerobic fungus *Scopulariopsis brevicaulis* is well documented [128–133] and is thought to involve methyl transfer via SAM [111]. Recently, the wood rotting fungus *Phaeolus schweinitzii* has also been shown to biomethylate antimony [134]. Undefined mixed cultures of bacteria growing under anaerobic conditions have been shown to generate volatile trimethylantimony [(CH₃)₃Sb] as the sole volatilized antimony species [135–137]. Volatilization of antimony from environmental sediments and municipal waste dumps also suggests that certain anaerobic and/or facultatively anaerobic bacteria can biomethylate [138, 139] this element. Recently, Michalke *et al.* [122] reported on the biomethylation of inorganic antimony by pure cultures of anaerobic bacteria. *C. collagenovorans*, *D. vulgaris* and three species of methanogenic archaea, were shown to produce trimethylantimony in culture headspace gases. Interestingly, *M. formicicum* was shown to generate stibine (SbH₃) into culture headspace gases, together with mono-, di and trimethyl antimony; previously only trimethyl antimony was detected as a biovolatilization product of antimony in headspaces of soil enrichment cultures and of pure cultures of *S. brevicaulis*. These authors [122] also reported the formation of trimethyl bismuth by pure cultures of *M. formicicum*, which may provide a microbial basis for the presence of this volatile compound in gases from municipal waste deposits and sewage gases [104, 105]. Environmental properties of organoantimony and-bismuth species are discussed in Chapters 7 and 8.

**Selenium**

The chemistry of arsenic and selenium are similar in many regards, and biomethylations of these two elements have much in common. Several fungi, including *S. brevicaulis* and a *Penicillium* sp, biomethylate selenium using
SAM as a methyl donor [140, 141]. Selenite, selenate and inorganic selenide have been shown to be biomethylated to the trimethyl selenium cation, via a pathway involving dimethylselenone [142] (Figure 1.8).

Some obligately aerobic bacteria have also been shown to methylate selenium and, in the natural environment, anaerobic bacteria are likely to contribute to this process [142]. The capacity to biomethylate selenium in microorganisms appears to be related to inorganic selenium resistance. The methylated forms of selenium are highly volatile and, like arsenic, biomethylation of selenium facilitates removal of selenium either as a water-soluble form or through (hydrophobic) volatilization. Microbial selenium methylation has been used successfully for in situ bioremediation of water and soil, resulting in removal of inorganic selenium (e.g. $\text{SeO}_4^{2-}$) through volatilization [143].

**Microbial demethylation/dealkylation**

For some metals, such as mercury and tin, microbial demethylation or dealkylation of organometallic forms are important reactions in detoxification mechanisms. Bacterial Hg(II) resistance, for example, involves reduction of Hg(II) to Hg(0) via mercuric reductase (MR). The reduced form of the metal is less toxic, more volatile, and is rapidly removed to the atmospheric compartment. Detoxification of organomercurials proceeds via organomercurial lyase (OL), a product of the *Mer B* gene, that enzymatically cleaves the Hg—C bond to form Hg(II), which is then removed via mercuric reductase [142, 144] (Equations 1.23 and 1.24). For example:

$$\text{CH}_3\text{Hg}^+ \xrightarrow{\text{OL}} \text{CH}_4 + \text{Hg(II)} \xrightarrow{\text{MR}} \text{Hg(O)}$$  \hspace{1cm} (1.23)

$$\text{C}_2\text{H}_3\text{Hg}^+ \xrightarrow{\text{OL}} \text{C}_2\text{H}_6 + \text{Hg(II)} \xrightarrow{\text{MR}} \text{Hg(O)}$$  \hspace{1cm} (1.24)

Bacterial oxidative demethylation of methylmercury, involving liberation of CO$_2$, also occurs. The mechanism is thought to involve enzymes associated with bacterial metabolism of C-1 compounds [145] and is believed to occur

![Figure 1.8](image-url)  
**Figure 1.8** Scheme for biomethylation of selenium. The methyl donor, S-adenosylmethionine, is illustrated as $R—\text{SCH}_3^+$.
widely in freshwater and aqueous environments, under both aerobic and anaerobic conditions.

Degradation of organotin compounds has been demonstrated for a wide range of microorganisms, including bacteria, fungi and algae [146]. Organotin degradation (Equation 1.25) is thought to involve sequential cleavage of tin–carbon bonds, resulting in removal of organic groups and a general reduction in toxicity [147–150]. Cleavage is initiated by hydroxyl attack.

\[
R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4
\]  

(1.25)

The wood preservatives tributyltin oxide (TBTO) and tributyltin napthenate (TBTN) have been shown to be degraded by fungal action to di- and monobutyltin. Certain Gram-negative bacteria and the green alga \textit{Ankistrodesmus falcatus} can also dealkylate tributyltins, giving rise to dibutyl, monobutyl and inorganic tin products; the alga was able to metabolize around 50% of the accumulated tributyltin to less toxic dimethyltin(IV) over a 4-week period [151]. Similar end-products are formed by the action of soil microorganisms on triphenyltin acetate [152]. Tin–carbon bonds are also cleaved abiotically, for example by UV light, and it has proved difficult to establish the relative importance of abiotic and biotic mechanisms of organotin degradation in the natural environment [146]. In some circumstances, environmental conditions (such as pH and redox potential), established by microbial activity, greatly influence the extent of abiotic degradation of organotins [146]. These comments relating to abiotic and biotic mechanisms of organotin degradation also apply to other organometal(loid)s. Environmental organotin chemistry is discussed in Chapter 3.

Bacterial demethylation of methylarsenicals is known to occur in aerobic aqueous and terrestrial environments, giving rise to CO₂ and arsenate [153]. Several common soil bacteria, such as \textit{Achromobacter}, \textit{Flavobacterium} and \textit{Pseudomonas}, have been shown to possess organoarsenical demethylation ability. Bacterial demethylation of methylarsenic acids excreted by marine algae is an important part of the biogeochemical cycling of arsenic.

Dimethylselenenide has been shown to be demethylated in anaerobic environments by methanogenic and sulfate reducing bacteria, with the liberation of CO₂ and CH₄ [78]. Several bacterial isolates form aerobic soils, including members of the genera \textit{Pseudomonas}, \textit{Xanthomonas} and \textit{Corynebacterium}, have been shown to utilize methylselenides as their sole source of carbon [154].

1.14 CORRELATION OF QUANTITATIVE STRUCTURE–ACTIVITY RELATIONSHIPS WITH ORGANOTIN MOLECULAR TOPOLOGY AND BIOACTIVITY

The concept of correlating the activity of a compound to one or more descriptors of the molecule is not new. Earlier correlations have mainly focused on organic systems. These types of correlation have been used extensively by the drug
industry. However, these types of relationship are also applicable to organometallic molecules, and organotin systems will be used to illustrate the concept here.

In the past several decades, there has been a dramatic rise in the production of organotin chemicals. The production of organotin compounds was 2000 tons in 1960 [155] and rose to more than 50,000 tons in 1983 [156]. In fact, there are more commercial uses of organotins than of any other organometallic system [157]. The increased usage of organotins is undoubtedly related to the diverse biocidal properties possessed by organotin compounds, discussed in more detail in Chapter 3. It is well established that the toxicity of organotin compounds is dependent on both the nature and the extent of alkylation or arylation of the tin atom (see Chapter 3).

The increased production of these chemicals as well as the formulation of new organotin compounds has led to increased concern about the fate of these compounds and their degradation products as environmental pollutants. Thus, the development of reliable correlations between the toxicities of organotins and some descriptor or descriptors of the molecule is of great value. It will allow the prediction of toxicities of new or untested compounds, and promote quantitative molecular designed prospects for safer industrial and medical applications.

A common technique used for relating structures of molecules to their toxicological activities is to develop a quantitative structure–activity relationship (QSAR). The quantitative structure–activity relationship is a regression equation that relates some measurable biological activity of a compound to some molecular descriptor or descriptors of the chemical. Molecular descriptors can be classified into four groups: physicochemical, topological, geometrical and electronic.

The various chapters of this work show that liquid chromatography provides a basis for both theoretical and practical assessments of fragmental or additive substituent contributions to molecular solution behaviour, including organotins as trace cations or neutral species. However, the introduction of a more complete approach using the molecule’s entire geometrical or electronic configuration was even more appealing [158]. This type of approach has been used in determining biological response in organic drug design [159]. With the rapid advances in current computer technology, the calculations of various topological descriptors for organometallic compounds is now commonplace. Among the leading topology descriptors are:

(i) Molecular connectivity. This is a bond-centred summation of electronegativity and electron density that is related to the molecular volume and valence state [160].
(ii) Branching index. This is a perturbational analysis of central and adjacent atoms that is related to the molecular refraction and volume [161].
(iii) Total surface area (TSA). This is computed using the Van der Waals radii of the atoms assuming a specific conformation for the molecule [162]. It is
related to the molecular volume and the hydrophobic solvent cavity or exclusion volume in polar solvents [161, 163].

The topological descriptors (molecular connectivity and TSA) correlate well with physicochemical properties of organic hydrophobic molecules that influence biological activity such as solubility [161, 164] partition coefficient [165], or solvent polarity [166]. In addition, estimates of simple molecular size or shape have proven accurate in predicting chromatographic retention for homologous series of toxic polycyclic aromatics [167], while refined connectivity indices correlate well with chromatographic retention of highly polar aliphatic compounds [168] or barbiturates [169]. For all those properties reported in common with the three molecular topology methods listed, correlation matrices indicate good agreement.

Bioconcentration factors (\(K_{B}\)) for aquatic organisms have been explained [170] in terms of the log \(P\) or aqueous solubility (\(S\)) for the cellular uptake of dilute solute molecules by organisms. Thermodynamic equilibrium is presumed and these techniques will be invalid if there is significant degradation of the molecule by any of the chemical or biological side reactions in the environment. However, the bioaccumulation of a wide range of organic compounds, including aliphatic and aromatic hydrocarbons, halides, acids and phosphate pesticides in fish has been linearly correlated [171] with the solubility (\(S\)) or log \(P\) value of the compounds and is given in Equations 1.26 and 1.27.

\[
\log K_{B} = m(\log S) + \text{constant} \quad (1.26)
\]
\[
\log K_{B} = m(\log P) + \text{constant} \quad (1.27)
\]

However, the specific uptake sites or route of entry of the chemical into the test organism cannot be stated with certainty based on these predictions. Lipophilic transmission is suggested due to the observed strong dependence of log \(P\). For large molecules, however, membrane permeation resistance is expected [170, 172].

Consistent with this picture, Wong et al. showed a direct correlation between the organic substituent (\(R\)), partition coefficient and the toxicity of triorganotin compounds towards algae [173]. Prior to the work of Brinckman et al., none of the topological descriptors had been applied to organometallic systems for predicting chromatographic retention or toxicity [174].

1.14.1 APPLICATION OF TOTAL SURFACE AREA (TSA) AS A PREDICATOR FOR ORGANOTIN COMPOUNDS

1.14.1.1 Additivity of Total Surface Area for Aqueous Solubility and Chromatographic Parameters

Total surface area (TSA) as a descriptor has been used because of its relevance and simplicity to stereochemical constructs of mono- and polynuclear core
structures as well as to the diverse number of organic substituents that is common to organometallic molecules. Organotin TSA values are easily calculated since a broad data base of bonding distances, angles and Van der Waals radii are readily available in the literature. Using these values, Brinckman et al. [175] were able to calculate the TSA values of various individual organotin molecules. Calculations for the individual molecules involved various degrees of coordination, charge or likely conformations (Figure 1.9) of the tin molecules. In addition to the calculation of the individual organotin molecules, the mean fragment TSA values for several organic groups (R) and labile inorganic ligands (Table 1.12) were also evaluated [174]. The mean fragment TSA values were calculated from either full tetra- or pentacoordinated triorganotin(IV) configurations. The use of mean fragment values as additive substituent TSA values along with a tin core structure TSA value may be subject to error due to the various conformations in organotin structures. This is because the TSA parameter has been shown to be sensitive to conformational changes [176]. In spite of this limitation, surprisingly good agreement with complete structure computer TSA calculations was obtained.

A good correlation, in the form of Equation 1.26 [177] was found between the TSA values for a series of methyl elements, (CH₃)ₓE, where E = Br, I, Hg, C, Sb and Sn, and their solubilities. Figure 1.10 shows that a good correlation was obtained between the solubility data for a series of tetraalkyl derivatives of group IV elements [177, 178] and their TSA values.

Brinckman et al. [175] were able to apply the TSA values to estimate the chromatographic retentivity for two series of mixed tetraorganotins. Two excellent linear correlations were obtained for the two classes of tetraalkyltin and arylalkyltin compounds. However, two distinct patterns of solvophobic behavior were observed with the conformationally flexible alkyl groups exhibiting far greater retentivity in the C₁₈ reverse bonded-phase column than the more rigid planar phenyl substituents.

Since the TSA parameter has been shown to be sensitive to conformational changes [176], the calculation of the TSA of the entire molecule would eliminate the problems encountered with fragmental values. To account fully for the various possible conformers of molecules, a ‘holistic’ approach was used by Eng et al. [179] for the calculation of the TSA values to estimate the capacity factors for a homologous series of group VA phenyl derivatives, (C₆H₅)ₓM. This approach would preserve the molecule’s entire geometric and/or electronic conformation. The term ‘holistic’ refers to a particular fixed conformation for the complete molecule and can distinguish the local carbon and M heteroatom geometries and their contributions to the overall TSA predictor. It does not necessarily imply that the TSA value for the whole molecule is more than the sum of its parts. This representative approach would distinguish the local carbon and the M heteroatom geometries. Using this approach, the authors were able to obtain a significant linear correlation between the capacity factors (ln k’) and the TSA values for only one particular set of conformers, implying preferred solute-column chemistry based on preferred C—M bond rotations. A
later study by Tierney et al. [180], using both mean fragment and holistic TSA calculations, found good correlations between TSA values and the natural logarithms of the capacity factors for both fluxional and rigid organotin systems as defined by summed carbon hybridization. Tie lines could be drawn
Table 1.12  Additive group/atom TSA values

<table>
<thead>
<tr>
<th>Organic group</th>
<th>TSA (Å²)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>32.7</td>
<td>0.02</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>55.4</td>
<td>0.01</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>74.4</td>
<td>1.6</td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>75.6</td>
<td>2.2</td>
</tr>
<tr>
<td>n-C₄H₉</td>
<td>95.4</td>
<td>1.8</td>
</tr>
<tr>
<td>i-C₄H₉</td>
<td>95.6</td>
<td>1.9</td>
</tr>
<tr>
<td>c-C₆H₁₁</td>
<td>117.9</td>
<td>2.2</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>92.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Inorganic group

<table>
<thead>
<tr>
<th></th>
<th>TSA (Å²)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>17.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Cl</td>
<td>27.6</td>
<td>2.3</td>
</tr>
<tr>
<td>CO₃</td>
<td>45.4</td>
<td>3.3</td>
</tr>
<tr>
<td>OH</td>
<td>20.2</td>
<td>0.05</td>
</tr>
<tr>
<td>OH₂</td>
<td>23.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>

---

a Mean TSA derived from 4- and 5-coordinate R₂Sn structures (cf. Figure 1.9)
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Figure 1.10  Solubility data for tetraalkyl derivatives of group IVA
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between the two systems. The use of these column-dependent tie lines allowed
the prediction of unreported compounds with mixed ligands.

Recently, Radecka [181] used the relative change of the trans-membrane
current to study the interaction of several organotin compounds with a gramici-
din ion-conducting channel. It was found that this parameter was relatable to the TSA of the compounds and the model presented may be applicable to the estimation of the toxicity of the compounds as well as other organometallic systems.

### 1.14.1.2 Molecular Topology Prediction of Organotin Toxicities in Aquatic Organisms

Several groups of mud crab larvae, *Rhithropanopeus harrisi* were exposed to seawater containing eight structurally distinct triorganotins for the duration of their zoaeal development by Brinckman *et al.* [175]. The results of this study indicated that there was a strong correlation between the LC₅₀ values (the concentration that causes 50% mortality) and the TSA values for the eight triorganotin compounds studied. A similar study was conducted for the analogous diorganotins [174]. The principal conclusions derived from the correlations of the LC₅₀ values with TSA values computed for each organotin toxicant were:

(i) High linear correlations existed between LC₅₀ values and the individually calculated TSA values [175] for either the tetra- or pentacoordinated triorganotin solvates or the chloroacetates of R₂SnCl(H₂O)ₓ⁻<sup>+</sup>

(ii) Only the mononuclear di- or triorganotin moiety appeared to be the rate-determining toxic agent.

(iii) A slightly better fit was obtained for the neutral triorganotin pentacoordinated hydrate forms over the tetracoordinated chloride, however, it was not significant at the 95% confidence level.

Using the additive TSA values in Table 1.12, Brinckman *et al.* were able to apply this approach to the study by Wong *et al.* [173] who determined toxicity data for freshwater algal species (*Ankistrodesmus falcatus*) from Lake Ontario. As before, only the neutral four- and five-coordinated triorganotin species gave excellent correlations between ln LC₅₀ and TSA. The chlorotin species is unlikely to form in freshwater, but from the values in Table 1.12, the distinction between –OH, –Cl or H₂O probably affects the quality of the line fit far less than the Sn—C bond angles and the accompanying number of labile inorganic groups in the tin’s inner coordination sphere. In a similar evaluation [174], the toxicity of a trialkyltin series towards spheroplasts obtained from *Escherichia coli* [182] was evaluated, and again it was found that TSA values from Table 1.12 correlated with the extent of bacterial organotin uptake.

A later study by Eng *et al.* [183] found a high correlation between TSA values and diorganotin toxicity towards several distinct types of organisms. The high correlation between the toxicities and the TSAs, which is independent of the cell type, suggests that it is the hydrophobic behaviour of the organotin species that governs the toxicity process in all cell types studied. The use of TSA as a predictor
of toxicity can be expanded to other organometallic systems. For example, Eng et al. [184] found a high correlation between the TSA values of triorganolead chlorides and their toxicity towards a bacterium (Escherichia coli) and an alga (Selenastrum capricornutum). A similar high correlation was obtained for the triorganotin chlorides. However, attempts to correlate other Group IVA organometals incorporating silicon or germanium as the metal center were unsuccessful due to the solubility of the compounds. A study on the inhibitory effects of alkyltin on anaerobic bacteria by Belay et al. [185] revealed that the TSA relationships observed with aerobic systems may not be valid for anaerobic systems. In a study on the organotin inhibition of methanogenic bacteria, Boppathy et al. [186] found that the inhibition of the bacteria increased with a decrease of the TSA value of the compound, which is in contrast to earlier studies. A similar negative correlation was reported by Lascourrèges et al. [187] in their study involving the toxicity of a series of organotins and three pure strains of sulphate-reducing bacteria.

A topological descriptor closely related to the total surface area of a molecule is the molecular volume. Since both of these descriptors are related to the radius of the molecule, Luedke et al. [188] were able to show that both the total surface area and molecular volume of a series of organotins can be used as a descriptor in QSAR studies with an equal level of confidence.

Brinckman et al. [175] were able to show in their aquatic toxicity studies that a high correlation existed between the TSA value of the organotin compounds and their LC50 values. Attempts to correlate the toxicity with descriptors that assign electronic and steric contributions of the molecule such as the ionic substituent constant (σ+) were unsuccessful [175]. These types of descriptor do not provide recognition of either geometric or configuration details that might influence the actual mode of transfer of the organotin species from the bulk solvent into the cell. The transfer most likely involves a reorganization zone, where only one n-alkyl group undergoes transition while the three stereochemically rigid R groups remain unaffected during the uptake process.

It should be noted that not all uptake processes on cells result in the transmission of the organotin. It was also shown that when the tri-n-butyltin cation was rapidly adsorbed on to the outer membranes of Gram-negative heterotrophic bacteria isolated from the Chesapeake Bay, essential metabolic processes continued unabated. Also, the bulk of the aquated tri-n-butyltin cation could be recovered unchanged by washing live cells with methanol. Such passive resistance to toxic metal-containing species by metal sorption is well known and has great environmental importance in metal biogeochemical cycles [189, 190]. It now remains to be seen whether such non-transmission can also be predicted by molecular topology methods, or whether some special geometrical features of the tin core and/or conformation of certain organic groups on the tin atom regulate the path and rates of these processes.
1.15 PRACTICAL CONSIDERATIONS

This section brings together into an environmental context the theoretical and experimental aspects of fundamental organometallic chemistry discussed above. Certain broad conclusions may be considered as follows.

(i) If an organometallic compound is detected in the atmosphere it must still be being inputted to the atmosphere (by a natural or anthropogenic process). So many routes to decay occur in the atmosphere that no organometallic compound would be detected if one was contemporarily being inputted.

(ii) The same, ultimately, holds true for organometallics detected in water, organisms or sediments. So many routes to decay exist that, ultimately, the organometallic would be eliminated. However, routes to decay here are shown (CH\textsubscript{3}Hg in humans is 70 days, butyltins are still being detected and high levels in and nearby to marinas long after they had been introduced).

(iii) Sediments in particular (anoxic, no light penetration) might be expected to stabilize organometallic compounds for longest—particularly as stabilizing coordinating ligands are amply present.

(iv) Non-compliance with the disposal regulations might account for confining presence of organometallics in water and sediments (e.g. butyltins) but inherently there is little citable evidence for this.

1.16 REFERENCES

20. Fox, M.F., De Montfort University, personal communication.
28. See Ref 5.
29. Ref. 5, pp. 50–52.
30. Ref. 5, pp. 71–73.
32. Ref. 5, pp. 90–95.
References
